The Kinetics and Solvent Effects on the Thermal Decomposition of Isopropyl Peroxide and 1,2-Dioxane.

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1. Abstract

Rates of H_2 formation have been determined for the thermal decomposition of isopropyl peroxide at 130°-150°C in toluene and methanol and at 140°C in isopropyl alcohol and water. Product studies have been carried out at 140°C in these solvents.

The decomposition of isopropyl peroxide was shown to be unimolecular with energies of activation in toluene, and methanol of 39.1, 23.08 Kcal/mole respectively.

It has been shown that the rates of H_2 formation in decomposition of isopropyl peroxide are solvent dependent and that the k_H vs "Z" values (parameters for solvent polarity) gives a straight line. Mechanisms for hydrogen production are discussed which satisfactorily explain the stabilization of the six-centered transition state by the solvent. One possibility is that of conformation stabilization by solvent and the other, a transition state with sufficient ionic character to be stabilized by a polar solvent.

Rates of thermal decomposition of 1,2-dioxane in tert-butylbenzene at 140°-170°C have been determined. The activation energy was found to be 33.4 Kcal/mole. This lower activation energy, compared to that for the decomposition of isopropyl peroxide in toluene (39.1 Kcal/mole) has been explained in terms of ring strain. Decomposition of 1,2 dioxane in MeOH does not follow a first order reaction.

Several mechanisms have been suggested for the products observed for decomposition of 1,2-dioxane in toluene and methanol.

2. Introduction

2.1 Studies on the thermal decomposition of alkyl peroxides (1,2) have shown that homolytic cleavage at the -O-O-bond is not the only path by which peroxides decompose. Hiatt, et al. (2) found that molecular hydrogen formed a significant product (25-30%) from the thermal decomposition of sec-butyl peroxide, and that H_2 plus Ph_2CO are the major products from $[Ph_2CHO]_2$ (6b).

This project has been mainly concerned with the mechanism of hydrogen formation in decomposition of secondary alkyl peroxides.

Three categories for the non-heterolytic decompositions of organic peroxides have been described.

The first is a unimolecular scission of the -O-O-bond.

Type (1) $$R\text{-}O\text{-}O\text{-}R \longrightarrow 2RO^{\cdot} \qquad (2.1)$$

The radicals can initiate a radical chain process or can disproportionate to give non-radical products.

The second is a concerted multiple bond homolysis exemplified by the prolyses of certain tert - alkyl peroxyesters (3).

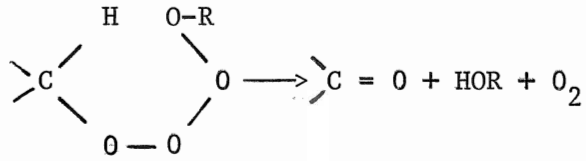
Type (2) $$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}R' \longrightarrow R^{\cdot} + CO_2 + {}^{\cdot}OR' \qquad (2.2)$$

Our focus of interest has been on a third type of decomposition thought to proceed via concerted cyclic six-center cleavage. Such reactions have been observed for several kinds of peroxides, but have the

common features that the alkyl group is non-tertiary and that a hydrogen α to the peroxide link is transferred in the reaction. Including in the type 3 category are:

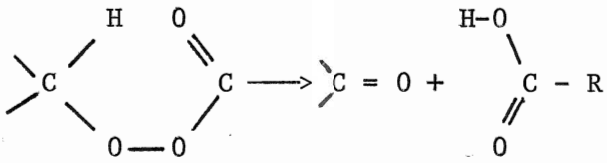
Type (3)

(a) Decomposition of non-tertiary alkyl tetroxides via the "Russell mechanism" (4).



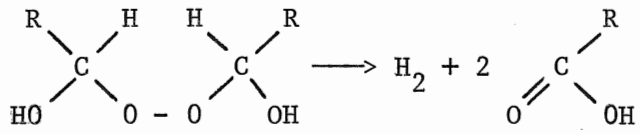
(2.3)

(b) Decomposition of non-tertiary-alkyl peroxyesters. (5)



(2.4)

(c) Decomposition of non-tertiary alkyl peroxides. (6,7)



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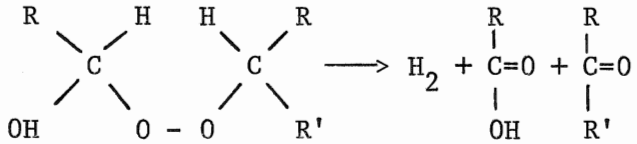

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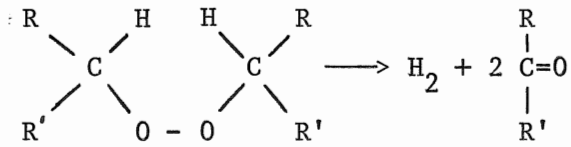
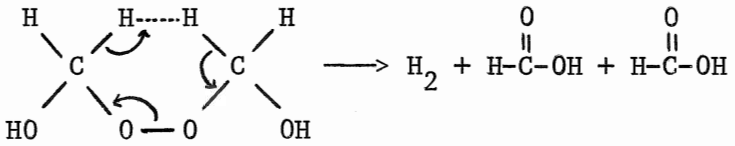


(2.7)

Each of the type 3 categories, (a), (b), and (c) has been extensively studied in its own right, and only recently have Hiatt, Gloves and Mosher (8) noted the connection between them in terms of another common feature: Type 3 reactions compete more or less effectively with Type 1 homolysis only in solution. In the gas phase Type 3 reactions compete ineffectively or not at all.

Since the work reported here concerns only the Type 3(c) reaction, the historical development will be similarly restricted.

Style and Summers (9) showed that in the photochemical reaction of formaldehyde and oxygen, bis-hydroxylmethyl peroxide was an intermediate. Decomposition of this compound in gas phase produced only 1-4% H_2 which is much less than the yield in condensed phase. They did not state any mechanism but later Jenkins and Style (10) for the decomposition of the very similar compounds, 1-hydroxyalkyl-alkyl peroxide proposed the six-center concerted mechanism.



$$\longrightarrow H_2 + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \qquad (2.8)$$

Wurster and Mosher (11) investigated the mechanism of decomposition of n-butyl-1-hydroxybutyl peroxide. The major products of decomposition of the neat liquid at 86°C were hydrogen, butyricacid, butyraldehyde, butyl alcohol and butyl butyrate. The minor products were propane, CO, butyl propionate, butyl formate and propyl butyrate which presumably were produced from free radical decomposition. They explained these observations by two different competitive pathways; (1), a major pathway which produced H_2, butyric acid and butyraldehyde directly,

$$C_3H_7CH_2\text{-}O\text{-}O\text{-}\underset{OH}{\underset{|}{C}}H\text{-}C_3H_7 \longrightarrow H_2 + C_3H_7\text{-}COOH + C_3H_7CHO \qquad (2.9)$$

, (2), a minor pathway which consisted of free radical reactions following the homolysis of the -O-O-bond,

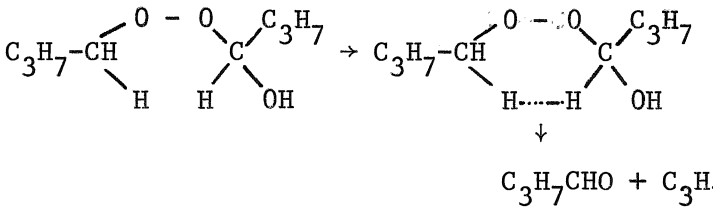
$$C_3H_7CH_2\text{-}O\text{-}O\text{-}\underset{OH}{\underset{|}{C}}H\text{-}C_3H_7 \longrightarrow C_3H_7CH_2O^{\cdot} + {}^{\cdot}O\text{-}\underset{OH}{\underset{|}{C}}H\text{-}C_3H_7 \qquad (2.10)$$

Wurster and Mosher checked more specifically for atomic hydrogen by hydrogen-deuterium exchange reaction (11).

$$H^{\cdot} + D_2 \longrightarrow HD + D^{\cdot}$$

Accordingly, the decompositon of n-butyl 1-hydroxbutyl peroxide was conducted in an atmosphere of deuterium and the result was compared to a blank of hydrogen, deuterium and tertiary-butyl hydroperoxide, which is known to give no hydrogen on decomposition (12) and a control containing cobaltocyanide ion which almost certainly reacts with water to evolve hydrogen in atomic form*.

The reaction of potassium cobaltocyanide with water, there was fifty times more exchange with deuterium than that of the peroxide. Furthermore, there was approximately the same amount of exchange in the blank containing the tertiary-butyl hydroperoxide. Thus Wuster, et al. rejected the idea of formation of atomic hydrogen during the reaction suggested by Rieche and Hitz (13). They proposed a concerted mechanism in agreement with the earlier suggestion of Wieland and Wingler (14).



$$C_3H_7CHO + C_3H_7COOH + H_2 \qquad (2.11)$$

The transition state in the concerted mechanism affords a lower energy of activation than the homolytic cleavage of the peroxide bond, perhaps because the transition is stabilized by various hyperconjugated forms (11).

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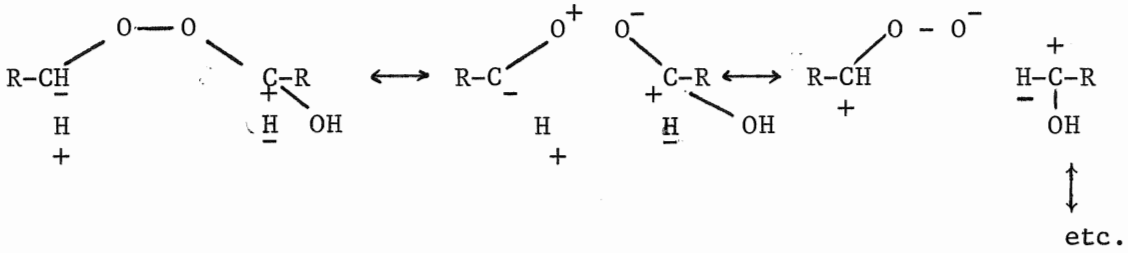
* Note: The hexacyano cobaltate II ion has a total of 37 electrons. The stable electronic arrangement is 36. Thus there is a strong tendency to lose one electron in reaction with H_2O or H^+ to give hydrogen atom and hexacyano cobaltate III ion

$$CO(CN)_6^{-4} + H^+ \rightarrow H^\cdot + CO(CN)_6^{-3}.$$



(2.12)

This proposed mechanism requires the reaction to follow first order kinetics. Durham and Mosher (5c) studied the kinetics and deuterium isotope effects on the thermal decomposition of 1-hydroxy-n-butyl n-butyl peroxide and 1-hydroxy-isobutyl isobutyl peroxide in α-methylstyrene, which was expected to be a satisfactory inhibitor for radical-induced decomposition, as well as in different other solvents. However, both hydrogen yields and first order rate constants depended on initial concentration of the peroxides. Since induced decomposition seemed unlikely in the presence of inhibitors, Durham and Mosher concluded that a solvent effect (15,16,17) of unknown nature contributed to the variation of the first order rate constants with initial concentration. The activation energies, 'A' factors and entropies of activation for thermal decomposition of 1-hydroxy-n-butyl n-butyl peroxide and 1-hydroxy-isobutyl isobutyl peroxide obtained in α-methylstyrene are shown in Table 1.

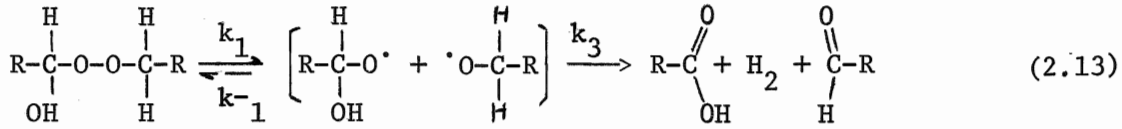
Table 1

Thermal Decomposition of 1-Hydroxy Peroxides (ref. 6c)

Peroxide	Ea Kcal/mole	A sec^{-1}	$\Delta S^{\ddagger}$ cals/mole /deg
1-hydroxy-n-butyl n-butyl peroxide	24.6	1.5×10^{10}	-15.7
1-hydroxyisobutyl isobutyl peroxide	21.2	2×10^{10}	-22

The quite low 'A' factors, (i.e., large and negative entropies of activation), suggested a rigid transition state. Such low 'A' factors have been repeatedly found for reactions postulated to proceed from non-cyclic reactants via a cyclic transition state (18). The validity of these numbers in Table 1 are questionable, however, since the reaction has shown deviation from unimolecularity.

An alternative to the concerted reaction is a "cage" mechanism (19) where radicals formed but react with each other within a solvent cage.



(2.13)

If k_1 is rate determining step then there would be only a small, secondary deuterium isotope effect when the corresponding deuterated compound was decomposed. Durham and Mosher (5c) have shown for decomposition of 1-hydroxyisobutyl-1-d-isobutyl-1,1-d_2 peroxide there is[a] kinetic isotope effect and calculated the k_H/k_D between 3.2-3.9, however, the peroxides they used were not isotopically pure. On the basis of this observation they rejected the "cage" mechanism.

More recently, Hiatt and co-workers have studied the thermal decomposition of secondary alkyl peroxides which generated H_2 plus a ketone competitively with -O-O-homolysis. Hiatt and Szilagyi (7a) showed that thermal decomposition of sec-butyl peroxide and the corresponding αα, dideuterated peroxide gave H_2 and D_2 respectively.

First order rate constants for the competing reactions in toluene solutions were measured, i.e., k_r for homolysis and k_H for hydrogen formation, and deuterium isotope rate effects were determined for each.

For k_r and k_H the k_H/k_D ratios were 1.47 and 1.68 respectively. The latter ratio seemed very small for a primary isotope rate effect and was not strong evidence for the cyclic mechanism.

Plots of log k vs. 1/T gave $k_H=10^{12}e^{-31000/RT}$ and $k_r=10^{15}e^{-35200/RT}$. The A-factor for k_H did not seem low enough to be convincing evidence for the cyclic mechanism.

Hiatt and Szilagyi also tested for a cage mechanism by conducting decomposition in mineral oil. Effects of solvent polarity were investigated by decomposing s-Bu_2O_2 and $[Ph_2CHO]_2$ in solvents other than toluene, including acetonitrile, nitrobenzene, tetrachloroethylene, benzene, cyclohexane, and perfluorokerosene.

The per cent yield of hydrogen was not affected by solvent viscosity or polarity. The results were more than a little perplexing since the no H_2 yield in the vapor phase seemed explicable only in terms of "cage" effect or polar character of the reaction.

As a last resort, Hiatt and co-workers suggested that subtle conformational effects might hold the key. Decomposition of a cyclic peroxide which would not have an unlimited number of conformers seemed worthwhile. At the same time it was recognized both that the earlier explorations of solvent effects had not embraced a very wide degree of polarity and that the conclusion drawn were not entirely warranted. Generally in exploring solvent effects only the per cent of H_2 yield had been measured. It is known that the rate of peroxide homolysis increases slightly with solvent polarity (20,21). Since the per cent of H_2 yield did not change, it was assumed that the transition state leading to H_2 was no more polar than the transition state leading to radicals, and that this result could be extrapolated to the vapor phase.

The objectives of this work were thus two-fold; (1), to examine the decomposition of a cyclic peroxide and (2), to do a thorough study of solvent effects on a well characterized acyclic peroxide. For the cyclic peroxide, 1,2-dioxane was chosen, it being the only non-tertiary cyclic alkyl peroxide known to be easily prepared. Moreover, its thermal decomposition had not been studied before and the facility with which the 6 membered ring, once ruptured, might be reformed seemed worth investigating.

For the acyclic peroxide, isopropyl peroxide was chosen. It had the virtue of not being decomposed in solution before, although gas phase data were available. Hopefully, it was polar enough to be soluble in water as well as solvents of lower polarity. As well, its high degree of symmetry has permitted a calculation of the expected A-factor for concerted decomposition to H_2 and acetone.

3. Experimental Section

3.1 Purification of solvents

All solvents used in this work were purified by distillation. The purity was checked by gas chromatography . The commercial "Chromatograde" toluene(99.9%) contained a trace amount of xylene isomers which did not interfere with the g.l.c. analysis.

3.2 Preparation of isopropyl peroxide.

Symmetrical dialkyl peroxides can be prepared in poor yield by alkylation of hydrogen peroxide with the corresponding alkyl methanesulfonate. The general preparative procedure is due to Mosher and co-workers (22). Peroxides used in this work were prepared by this general method. Pryor and co-workers (23) have suggested a modification which they have claimed to give higher yields and which involved distillation of peroxide at 71 mm Hg as soon as it is formed into receiving flask which was kept at 0°C. Use of the Pryor modification in this work did not result in higher yields. The cause of poor yield is known. Both alkyl methanesulfonate and the peroxide are unstable in the strong basic medium used in the Mosher method and decomposition of both starting material and products competes with the accumulation of peroxide.

3.2.1 Preparation of isopropyl methanesulfonate

A mixture of 114.5 gm (1 mole) of CH_3SOCl and 60 gm (1mole) of isopropyl alcohol was cooled to 0-5°C and 158 gm (2 mole) of pyridine (previously dried over KOH and distilled), was added over 3.5 hours with stirring. Stirring was continued for half an hour. The reaction mixture was then added to 625 cc of 10% ice-cooled HCl and the product extracted with 375 cc ether. The ether layer was washed with two 100 cc portions of H_2O followed by 150 cc

of saturated sodium bicarbonate solution. The ether solution was dried over anhydrous potassium carbonate. Ether was removed under vaccum at room temperature. The residue was distilled at 2 mm Hg between 77-80°C. The yield was 110 gm or 79% of theoretical.

3.2.3 Preparation of isopropyl peroxide

A mixture of .6 mole of isopropyl methanesulfonate (82.8 gm), 0.3 mole (33.4 gm) of 30% H_2O_2 and 20 cc MeOH was cooled to 0-8°C. 0.6 mole of 50% aqueous KOH was added over 30 minutes with vigorous stirring. The reaction mixture was allowed to come to room temperature. After five hours a second addition of .15 mole (17 gm) of 30% H_2O_2 was added and the reaction was allowed to stir for 15 hours. The reaction mixture was worked up by adding water in order to dissolve the potassium methanesulfonate, extracting the aqueous solution with three portions of 50 cc of pentane and washing the combined extracts with 30 ml 5% KOH to remove hydrogenperoxide formed during the reaction. The pentane solution was then washed with distilled water until the washings were neutral, and dried over anhydrous sodium sulfate. Pentane was removed by distillation at slightly reduced pressure (36°C) and the residue was distilled through an 8-inch column packed with glass helices. The peroxide boiled between 55-58°C at 233 mm Hg. The first distillation yielded 90% pure peroxide. Three distillations were required to yield 99.9% pure peroxide. The purity of peroxide was determined by gas chromatography using a column packed with 5% SE-30 on Chromosorb W 80-100 mesh. Yield; 4.2 gm, 12%.

3.3 Preparation of 1,2-dioxane

1,2-dioxane was prepared by the R. Criegee and G. Müller (24) modification of the Mosher procedure. They used the appropriate alkyl

methanesulfonate, $(MeSO_3CH_2CH_2)_2$, for alkylation of H_2O_2 in presence of KOH, and claimed 30% yield. Following their method, not more than 15% yield was obtained. Addition of the KOH had to be very slow; otherwise the main product was tetrahydrofuran. Another by-product formed during the reaction was identified by M.S. and n.m.r. as $CH_3O(CH_2)_4OH$. This product could be produced by base catalysed decomposition of starting material.

3.3.1 Preparation of $MeSO_3(CH_2)_4O_3SMe$

29.7 gm (0.33 mole) of 1,4 butanediol and 68.4 gm (0.6 mole) of $MeSO_2Cl$ were mixed in three necked flask equipped with thermometer, mechanical stirrer and dropping funnel. 94.8 gm (1.2 mole) of dried pyridine was added over 5 hours from dropping funnel while keeping the reaction flask at 25-30°C. When about half of the pyridine was added crystals started to form and after a while the contents of the flask was mainly a solid material which was difficult to stir, even with a mechanical stirrer. Stirring was continued for one more hour. The reaction mixture was poured into 450cc ice-cooled 2N HCl, and cooled in a refrigerator for one hour. The white crystals which formed were filtered and recrystallized several times from 95% EtOH to give pure product. Yield; 48.7 gm (60%), m.p. 119°C, (Literature 119°C) (24).

The n.m.r. of this compound consists of a multiplet centered at 1.9 p.p.m., a multiplet centered at 4.20 p.p.m. and a singlet at 3.0 p.p.m. with the intensity ratio of 4:6:4.

3.3.2 Preparation of 1,2-dioxane

In a three-necked flask equpped with condenser, dropping funnel and thermometer, 29.6 gm (.12 mole) of the bis-methanesulfonate, 60 ml MeOH, 60 ml 50% H_2O_2 and 2 gm anhydrous $MgSO_4$ were mixed with a few drops of thymol blue. The mixture was warmed to 60-70°C. While stirring the solution strongly, a solution of 20% KOH in MeOH was added from a dropping

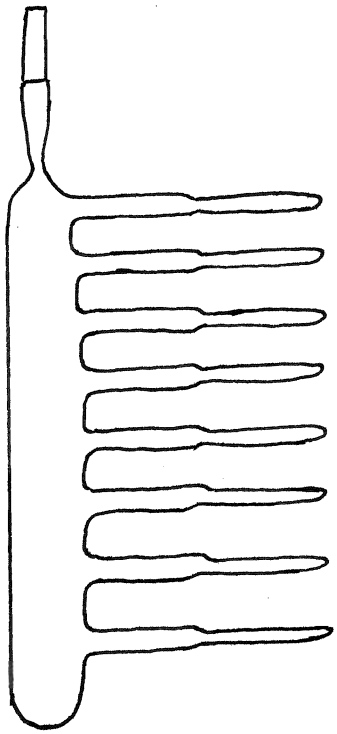
funnel at such a rate that the thymol blue indicator stayed in yellow-yellow green range. A total of 68 ml of the KOH solution was used. Slow addition of the KOH solution was required. The best result was obtained when the base was added over 6 hours. At the end of reaction, the mixture was cooled, 80 ml of H_2O was added and the mixture was filtered to remove solids. The solution was extracted with four 40 ml portions of CH_2Cl_2. The CH_2Cl_2 solution was dried over anh. $MgSO_4$ and distilled at reduced pressure in 4"Vigreux column and 8" column packed with glass helices respectively. The fraction which boiled at 55-65°C/110 mm Hg was collected and redistilled. Collecting the fraction boiling at 62.5-61.5°C/110 mm Hg (Lit. value(24), 61.5°C/110 mm Hg.) showed by g.l.c. analysis using a 6 foot 1/8" column packed with 10% isodecyl phthalate on Chromosorb W ; the product to be contaminated with tetrahydrofuran and another impurity later shown to be the mono-methyl ether of 1,4-butanediol. The highest purity of 1,2-dioxane obtainable by distillation was 80%.

"Pure" 1,2-dioxane (96%) was obtained by preparative g.l.c. using 4 foot 1/2" column packed with 20% di-isodecyl phthalate on Chromosorb W (80-100 mesh). Yield; 1.5 gm 15%. The n.m.r. spectrum of pure 1,2-dioxane consists of a multiplet at 1.8 p.p.m. and a multiplet at 4.2 p.p.m. with intensity ration of 4:4.

3.4 Rate measurements

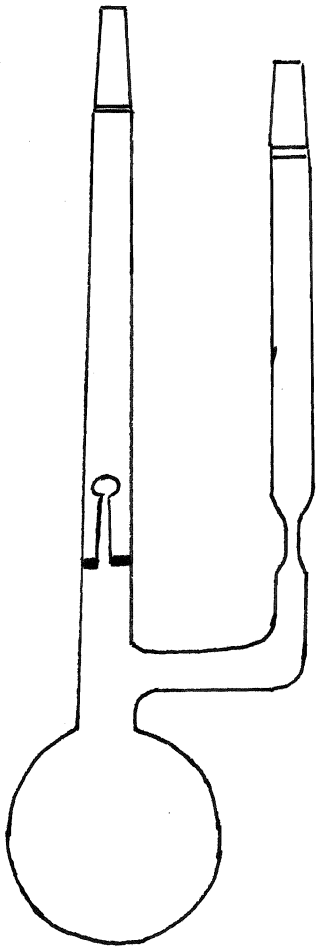
Kinetic experiments were carried out in sealed, degassed ampoules which were prepared by filling a "pig" (Figure 1) with about 10-15cc (depending on the size of the pig) of the peroxide solution of known concentration.

The "pig" was connected to vacumm line. The solution was cooled with liquid nitrogen until it became solid and then pumped for half an hour. After this period, the liquid nitrogen was removed and the



"Pig"

(Figure 1)



(Figure 2)

solution was warmed to room temperature. This process was repeated two more times. After degassing, ampoules were filled with the solution and sealed. These ampoules were immersed in a constant temperature oil bath and were withdrawn at appropriate intervals. G.l.c. analysis was used to determine the concentration of the unreacted peroxide and of the products.

Specific conditions for each peroxide in the several solvents used, i.e., columns, temperatures, flow rates, retention times and internal standards are given in Appendix I.

3.5 Product analysis

In each run 10 cc of known concentration of peroxide placed in a bulb equipped with break-seal, (Figure 2) degassed and sealed. The bulb was immersed in a constant temperature bath until complete decomposition had occurred. (The time of heating was equivalent to 10 half-lives or more.) After the reaction, these bulbs were placed to vacumm and cooled down by liquid nitrogen. Non-condensable gases were transferred by a Toepler pump to a segment of the line having a known volume and the total pressure and temperature were measured. This line segment was directly connected to the gas-inlet valve of an F&M model 700 Gas Chromatograph.

3.6 Analysis of gaseous products

The analysis of all gaseous products was carried out on a column packed with molecular sieve 13X and activated by heating at 300°C and passing carrier gas through for two hours. This column could separate all the gases and gave sharp peaks. Since the main goal of the gas analysis was to measure H_2 yields accurately, argon was used as carrier gas. Thermal conductivities of argon(3.88 cal/cm-sec/deg.)(25) and H_2 (39.60) are quite different so that the response for H_2 is much larger

than if helium (33.60) is used. The peak area of H_2 is not linear with concentration, however, and it was necessary to plot calibration curves. Although using argon as carrier gas causes the response for CO(5.425) and CH_4(7.20) to be small, these can be measured accurately by using higher sensitivity. No attempt was made to measure ethane which one would expect to be produced by combination of two methyl radicals.

With a 6 foot x 1/4" column at room temperature and argon flow of 25 ml/min., retention times were: H_2, 2.3 min.; CH_4, 6.8 min.; CO, 8.6 min.

After the non-condensables had been toepled off, the vacumm line was evacuated, the contents of the bulb were brought to room temperature, cooled down again with liquid N_2 and opened to vacumm line. In no case was a measurable pressure observed. To check further, at the end of every analysis the liquid was brought up to room temperature, opened to vacumm line and the vapor analysed. In no case was a significant amount of H_2 or CH_4 found.

It was important to be sure that the method of separating the non-condensable gases from the other products did not leave significant amounts of the non-condensables dissolved in the frozen solution.

3.7 Analysis of other products

After the removal of gases, the remaining solution was analyzed using a Varian aerograph series 1200 F.I.D. gas chromatograph. Peak areas were measured by electronic integrator model HP 3370B. Each determination was done in triplicate and internal standard was used routinely. Necessary correction factors relating peak area ratios to mole ratios were determined from known mixtures of each component with

with appropriate internal standards. Details of the analyses of products from isopropyl peroxide are given in appendix II.

3.8 Products from the decomposition of 1,2-dioxane in toluene.

A sample of peroxide in toluene (.1161 mole/lit) was degassed and decomposed at 150°C for 682 min. G.l.c. analysis using 6 foot x 1/8" column packed with carbowax 1500 on Chromosorb W (80-100) at flow rate of 25 ml/min. and column temperature of 55°C gave only one peak, retention time of 2.3 min.

It was suspected that this product might be $HO(CH_2)_3CHO$, and an i.r. spectrum of the product solution showed both OH (3575 cm^{-1}) and C=O (1725 cm^{-1}). G.C./mass analysis, however, gave no peaks corresponding to the molecular ion or reasonable fragments. It was suspected that the material did not pass through the separator. Treatment of the product solution with 2,4-dinitrophenylhydrazine did yield a precipitate. Mass spectrometric analysis of this using the solid probe gave a peak at m/e=286 which corresponds to the molecular ion of $HO(CH_2)_3CH{=}N{-}NH{-}C_6H_3(NO_2)_2$.

4. Results

4.1 Rates of decomposition of isopropyl peroxide

Thermal decomposition of isopropyl peroxide was carried out at temperatures of 110-150°C in four solvents, toluene, methanol, isopropyl alcohol and water at initial concentrations ranging from .1583 [M] to 6.6×10^{-5} [M]. Rates were measured by g.l.c. determination of the percentage of remaining peroxide in each case.

Plots of $\log[\text{i-pr}_2\text{o}_2]$ vs. time were linear (Figure 3,4,5). First order rate constants, determined from the slope of these lines, are shown in Table 2,3,4. In toluene rate constants were not dependent on the initial concentration showing that the reaction was truly unimolecular and that induced decomposition is probably not very important.

Activation energies were obtained from plots of log k vs. $1/_T{}^{\circ}k$ (Figure 6,7) and found to be 39.1 and 23.08 Kcal/mole in toluene and MeOH respectively.

4.2 Rates of decomposition of 1,2-dioxane

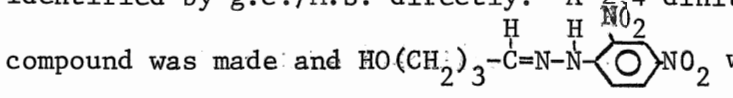
Thermal decomposition of 1,2-dioxane was carried out at temperatures between 140-170°C in two different solvents with initial concentration of .220 [M] in tert-butylbenzene and .2186 [M] to .117 [M] in MeOH. Plots of log[peroxide] vs. time were linear in t-Bu-  (Figure 8).

The rates of decompositions and energy of activation are given in Table 5. Activation energy obtained from plot of log k vs. $1/_T{}^{\circ}k$ (Figure 9) and found to be 33.4 Kcal/mole. Decomposition of 1,2 dioxane in MeOH at 140°C at two different initial concentrations were not first order (Figure 10) and it seemed that another mechanism governed this system.

4.3 Products of decomposition of isopropyl peroxide in the liquid phase

Both gaseous and liquid products of the thermal decomposition were analyzed by g.l.c. The analysis was carried out by taking 10 cc samples of a known concentration of peroxide in a given solvent and heating these for at least 10 half lives. First the contents of the flask were analyzed for gases and later for liquid products. Liquid product studies were done only at 140°C in the four solvents, but H_2 yield was measured between 130°-150°C. Table 6 shows products of thermal decomposition of isopropyl peroxide in ϕCH_3, $(CH_3)_2CHOH$, MeOH and H_2O at 140°C. In MeOH a trace amount of HCHO was found which was not measured quantitatively. The yield of H_2 in different solvents with different polarity between 130-150°C are shown in Table 7. For finding a relation between solvent polarity "Z" (Kosower parameter for solvent polarity) and the rate of hydrogen formation, the results from previous tables are collected in Table 8, which also gives values for k_r and k_H*. Plot of log k_H vs. "Z" gives a perfectly linear correlation (Figure 11), although the plot of k_r vs. "Z" does not appear as a straight line (Figure 13). Tables 9, 10 present Arrhenius parameters for decomposition of isopropyl peroxide in toluene and MeOH respectively. Plots of k_r and k_H vs. $\frac{1}{T°k}$ in ϕCH_3 and MeOH are shown in Figure 14-17.

4.4 Decomposition products of 1,2-dioxane in ϕCH_3

The only product which was formed during the decomposition of 1,2-dioxane in toluene was $HO(CH_2)_3CHO$. This compound could not be identified by g.c./M.S. directly. A 2,4 dinitrophenylhydrazone of this compound was made and  was identified by M.S. No

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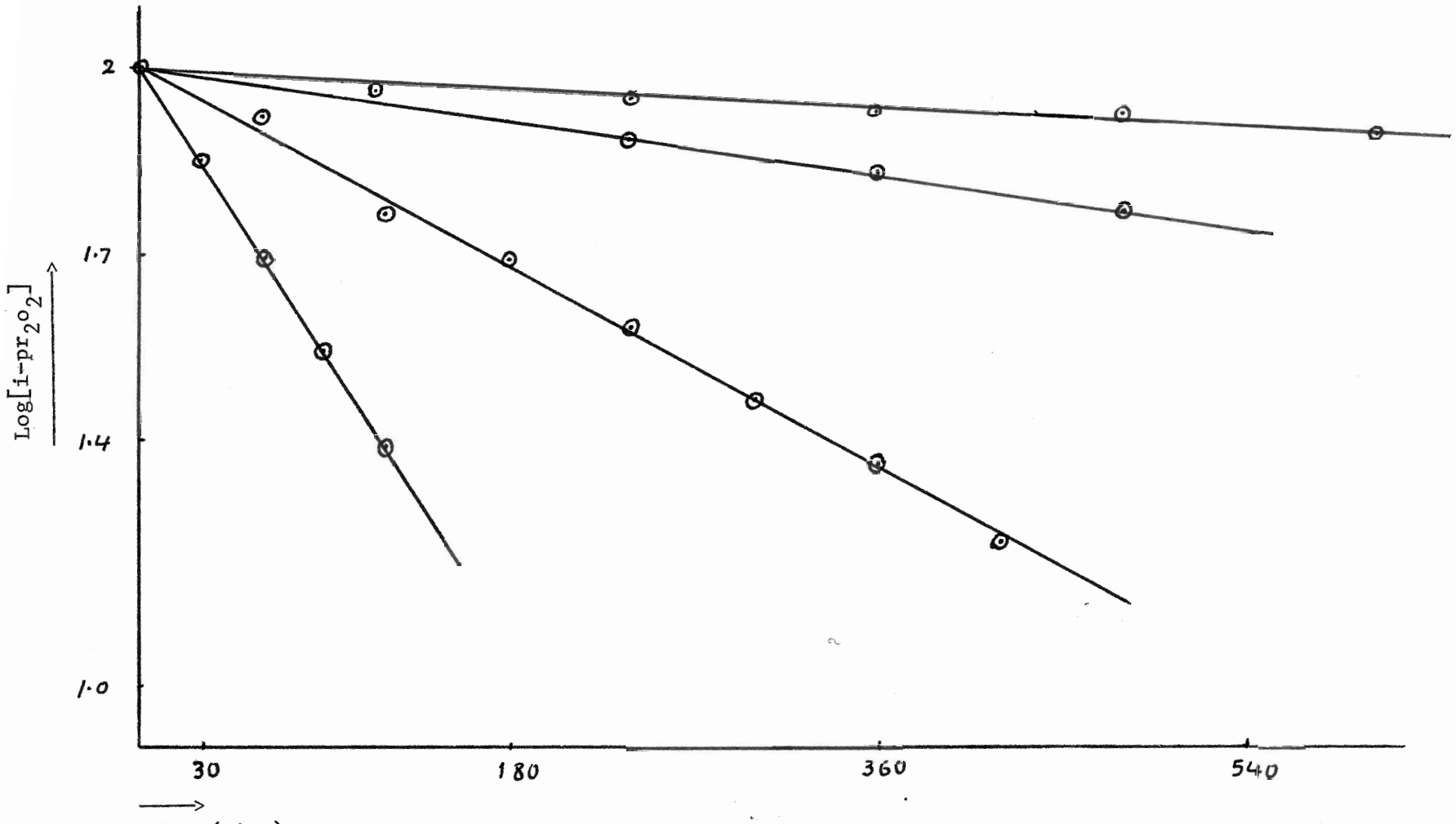
* Rate constants for decomposition to free radicals and to H_2, respectively. These are calculated from k_D and the H_2 % yield, assuming that both reactions are first-order in peroxide.

bibenzyl and 1,4 butanediol were found. The yield of H_2 was very low (∿1%) and it was the only gaseous product which was found.

5.5 Decomposition products of 1,2-dioxane in MeOH

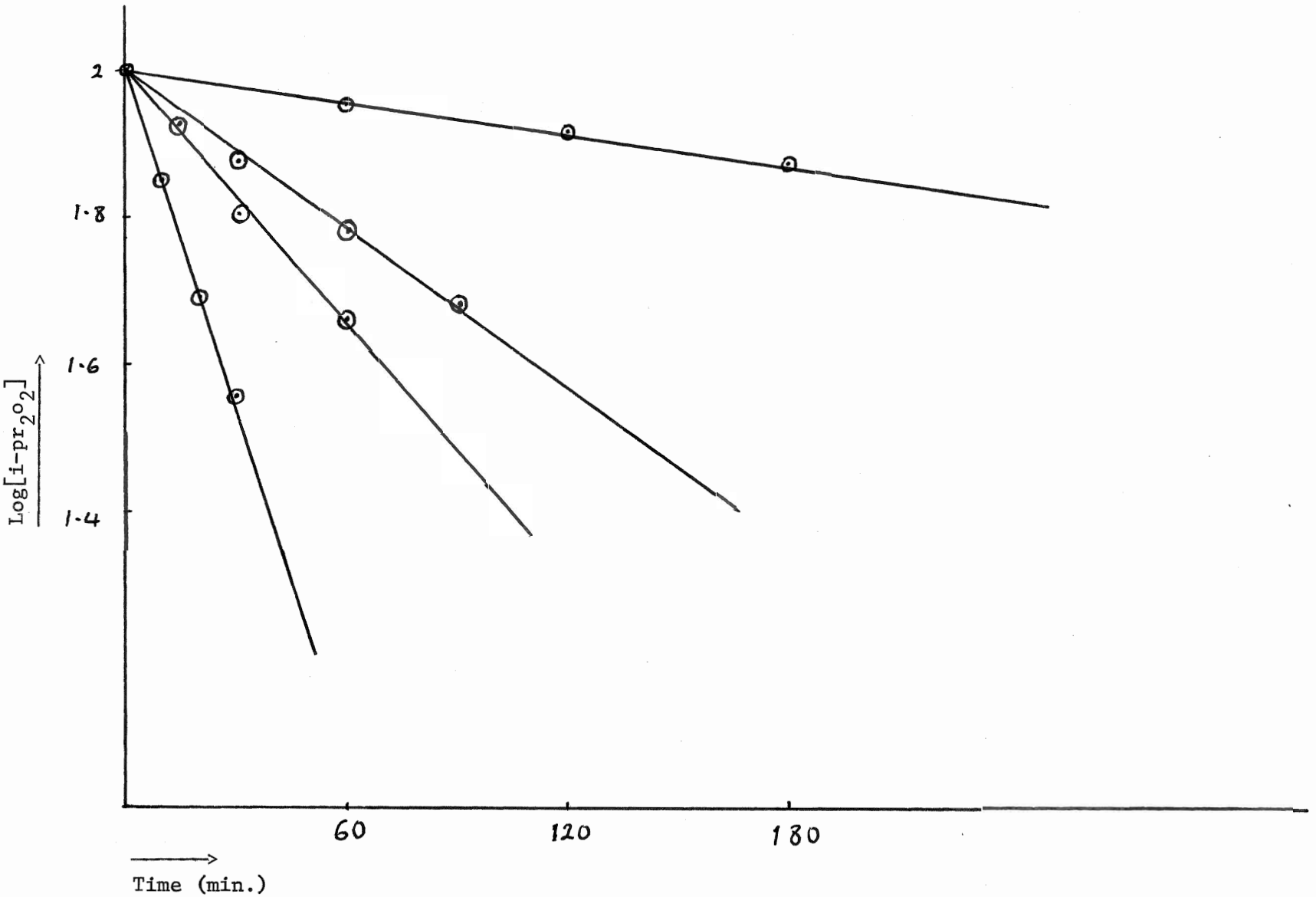
The liquid products of decomposition of 1,2-dioxane in MeOH were identified by g.c./M.S.. A major product with very close retention time to peroxide on 10% di-isodecylphthalate column was identified as  CHOMe. Another product which eluted rapidly from the g.l.c. column, and which was shown by mass spec. to have a molecular weight of 46 could have been CH_3OCH_3. The hydrogen yield was very low and was estimated to be 0.3 to 0.4%. No other products were found.

(Figure 3)



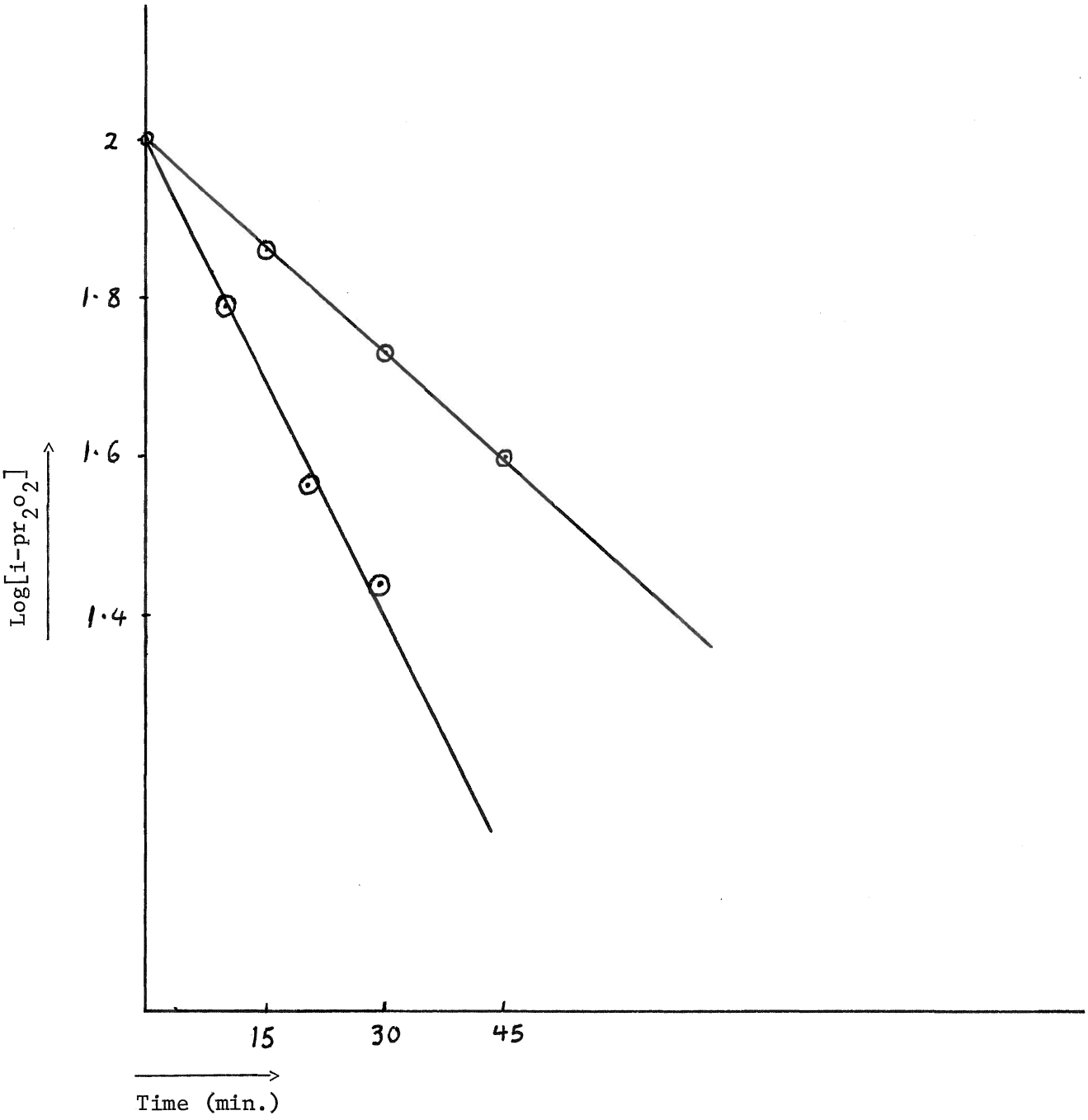
First order plots for decomposition of isopropyl peroxide in toluene at 120°-150°C. Initial concentration ranging from .1583 to .0875 mole/l .

(Figure 4)



First order plots for the decomposition of isopropyl peroxide in MeOH at 110°-150°C. Initial concentration .1419 mole/1

(Figure 5)



First order plots for decomposition of isopropyl peroxide at 140°C.
(1) in $(CH_3)_2CHOH$, initial concentration of 0.1524 mole/l
(2) in H_2O, initial concentration of 6.6×10^{-5} mole/l

Table 2

Rate constants for the thermal decomposition of isopropyl peroxide in toluene

Temp. °C.	Conc. [M][a]	Time int.[b]	K x 10^6[c] sec^{-1}	Ea Kcal/mole[d]
120	.1315	2 Hr.	5.66	
130	.1583	2 Hr.	18.88	
	.0969		18.27	
				39.1
140	.1196	1 Hr.	65.8	
	.1196		69.6	
	.0875		65.6	
150	.1196	½ Hr.	194.1	
	.0909		201	

[a] Initial concentration of i-pr_2O_2 in mole/l.

[b] Time interval between samples.

[c] First order rate constants.

[d] Arrhenius energy of activation.

Correlation co-efficient = 0.999

Table 3

Rate Constants for the thermal decomposition of isopropyl peroxide in MeOH.

Temp. °C.	Conc. [M][a]	Time int.[b]	k x 10^6 sec^{-1} [c]	Ea Kcal/mole
110	.1419	60 min.	27.5	
130	.1419	30 min.	127.5	23.08
140	.1419	30 min.	219.8	
150	.1419	10 min.	533	

[a] Initial concentration of i-pr_2o_2 in mole/l.

[b] Time interval between samples.

[c] First order rate constants.

[d] Arrhenius energy of activation.

Correlation coefficient = 0.999

Table 4

Rate constants for the thermal decomposition of isopropyl peroxide in i-PrOH and H_2O at 140°C

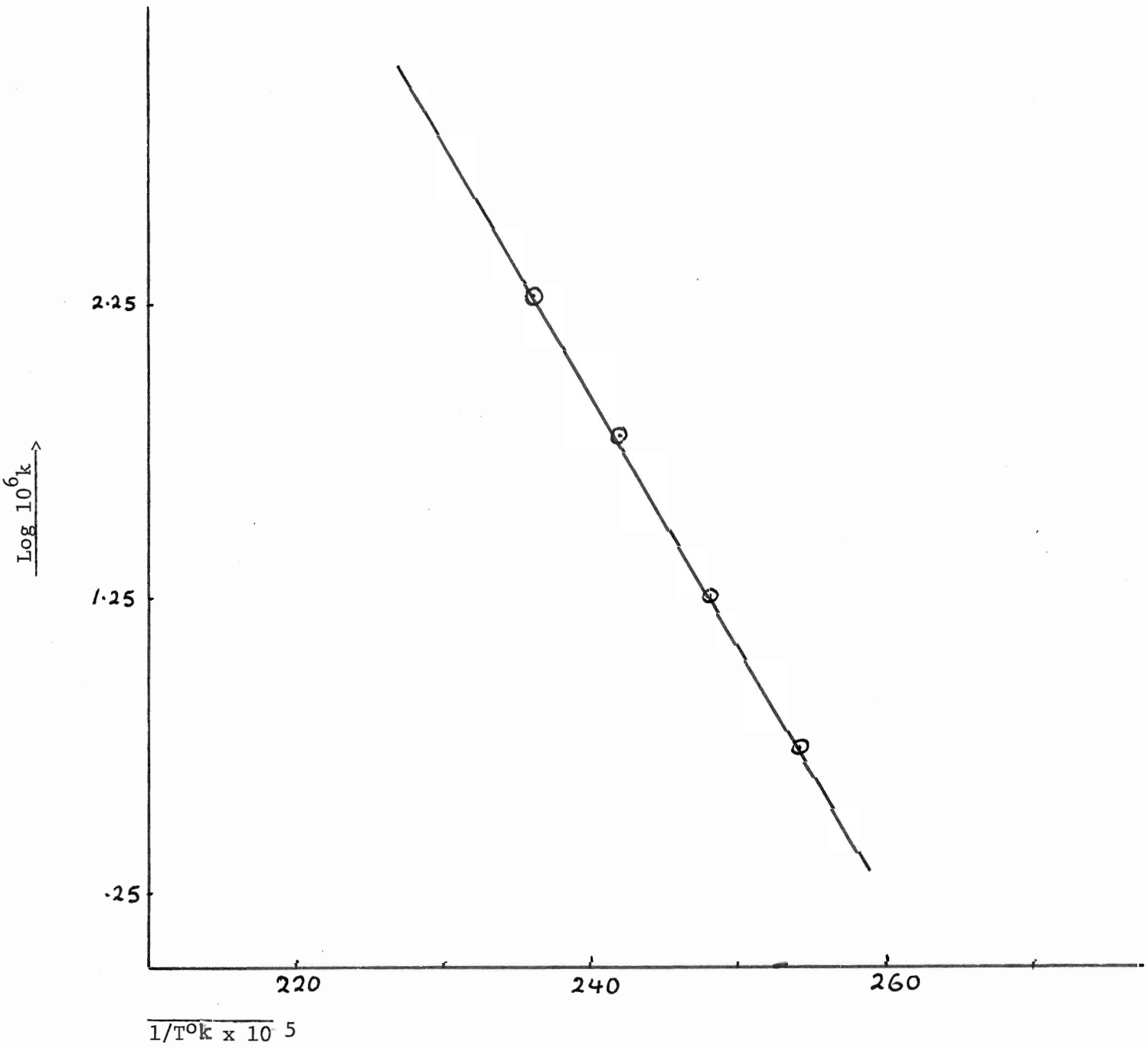
Solvent	Temp. °C	Conc. [M][a]	Time int.[b]	k x 10^6 [c] sec^{-1}
i-PrOH	140	.1524	15	339
H_2O	140	6.6 x 10^{-5}	10	715

[a] Initial concentration of i-pr_2o_2 in mole/l.

[b] Time interval between samples.

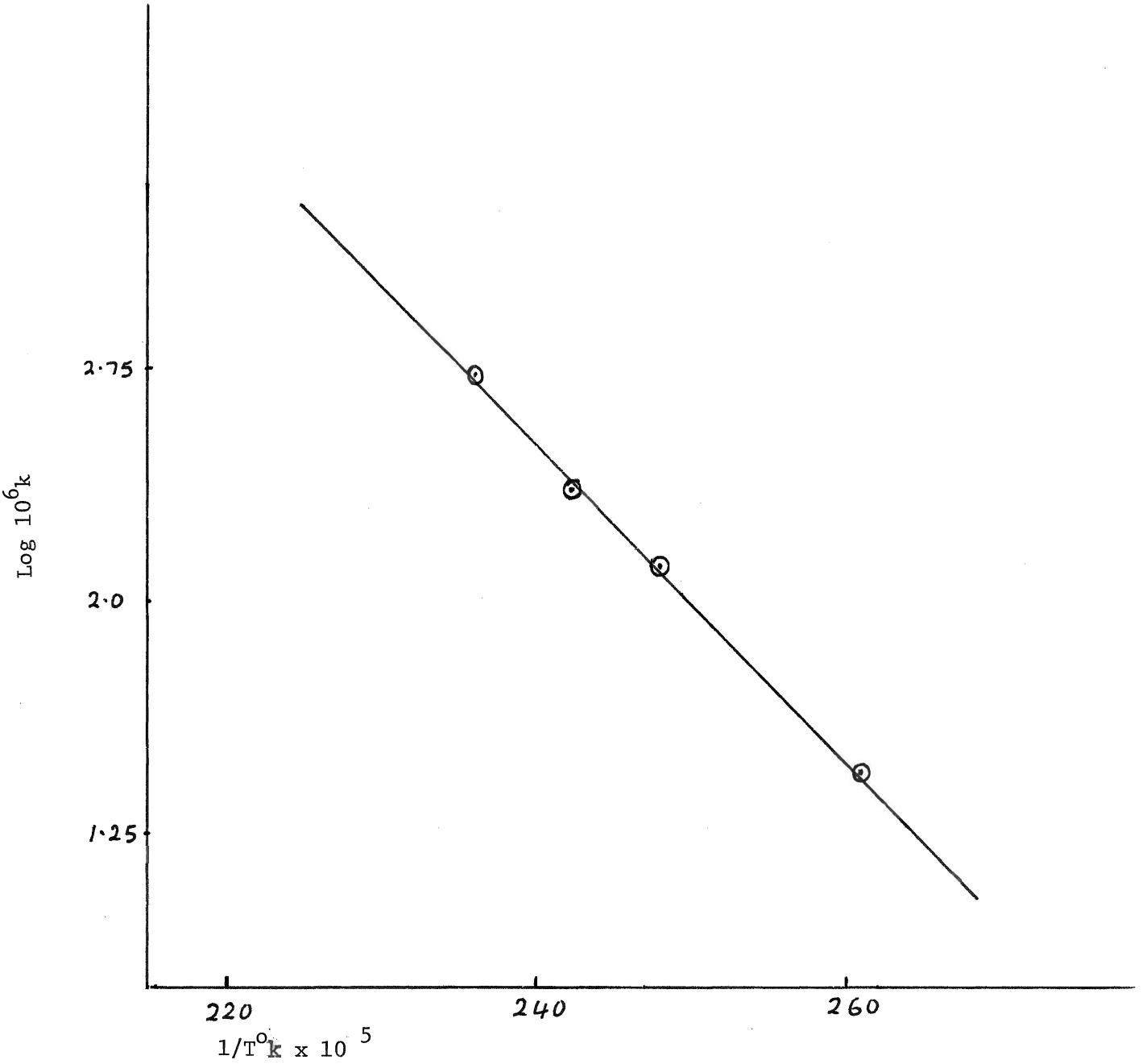
[c] First order rate constants.

(Figure 6)



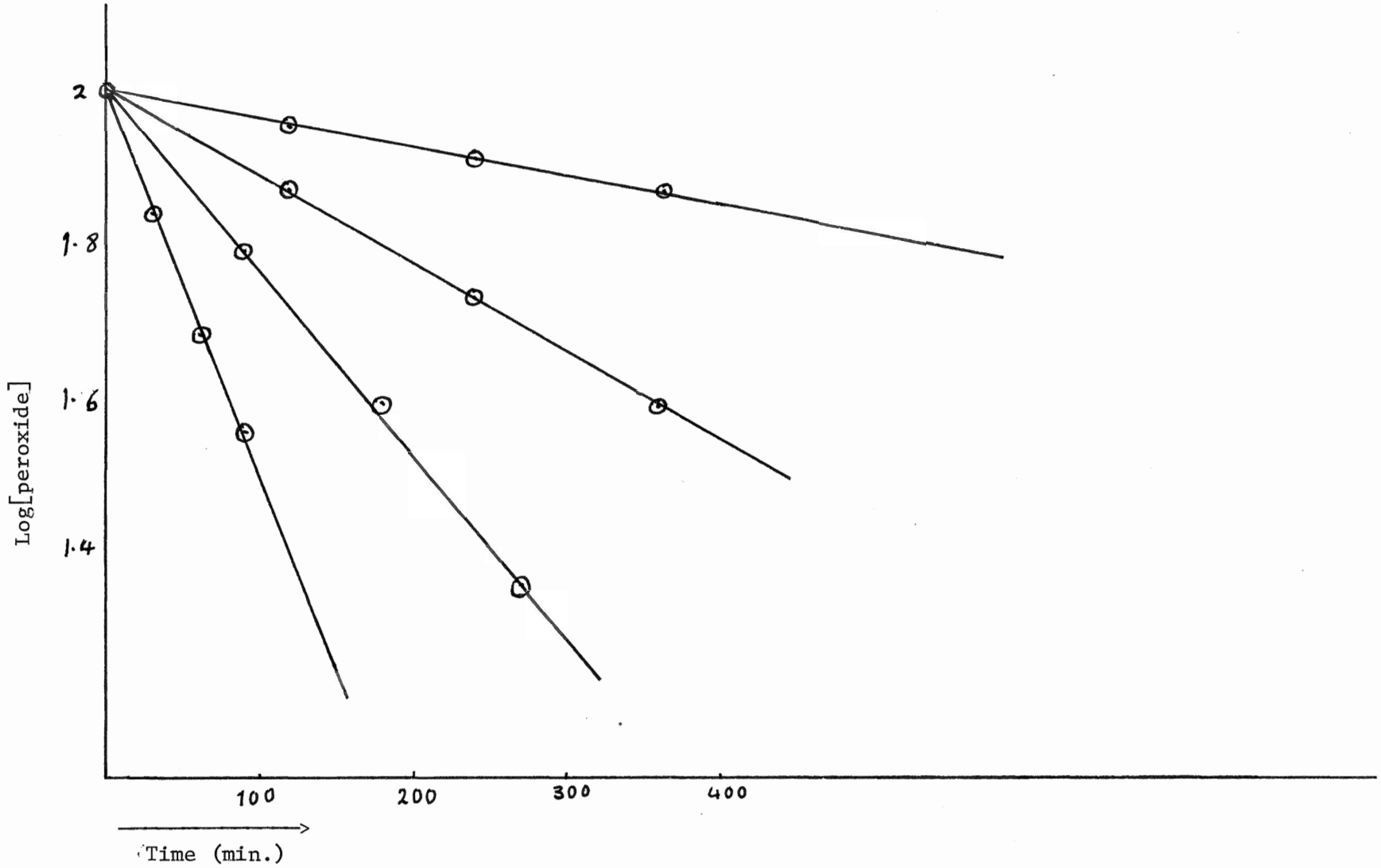
Arrhenius energy of activation for decomposition of isopropyl peroxide in toluene

(Figure 7)



Arrhenius energy of activation for decomposition of isopropyl peroxide in MeOH

(Figure 8)



First order plots for the decomposition of 1,2 dioxane in tert-butylbenzene at 140°-170°C. Initial concentration of 0.220 mole/l.

Table 5

Rate constants for the thermal decomposition

of 1,2 dioxane in tert-butylbenzene

Temp. ^{o}C	Conc. [M][a]	Time int.[b]	$k_d \times 10^{6}$[c] sec^{-1}	$k_H \times 10^{6}$[d] sec^{-1}	$k_r \times 10^{6}$[e] sec^{-1}	$\log_d A$[f] sec^{-1}	Ea[g] Kcal/mole
140	.220	2 Hr.	13.2				
150	.220	2 Hr.	44.0	.44	43.56	12.73	33.45
160	.220	1½ Hr.	94.3				
170	.220	½	206				

[a] Initial concentration of 1,2 dioxane in mole/1.

[b] Time interval between samples.

[c] Overall first order rate constants.

[d] Rate of H_2 formation at 150°C.

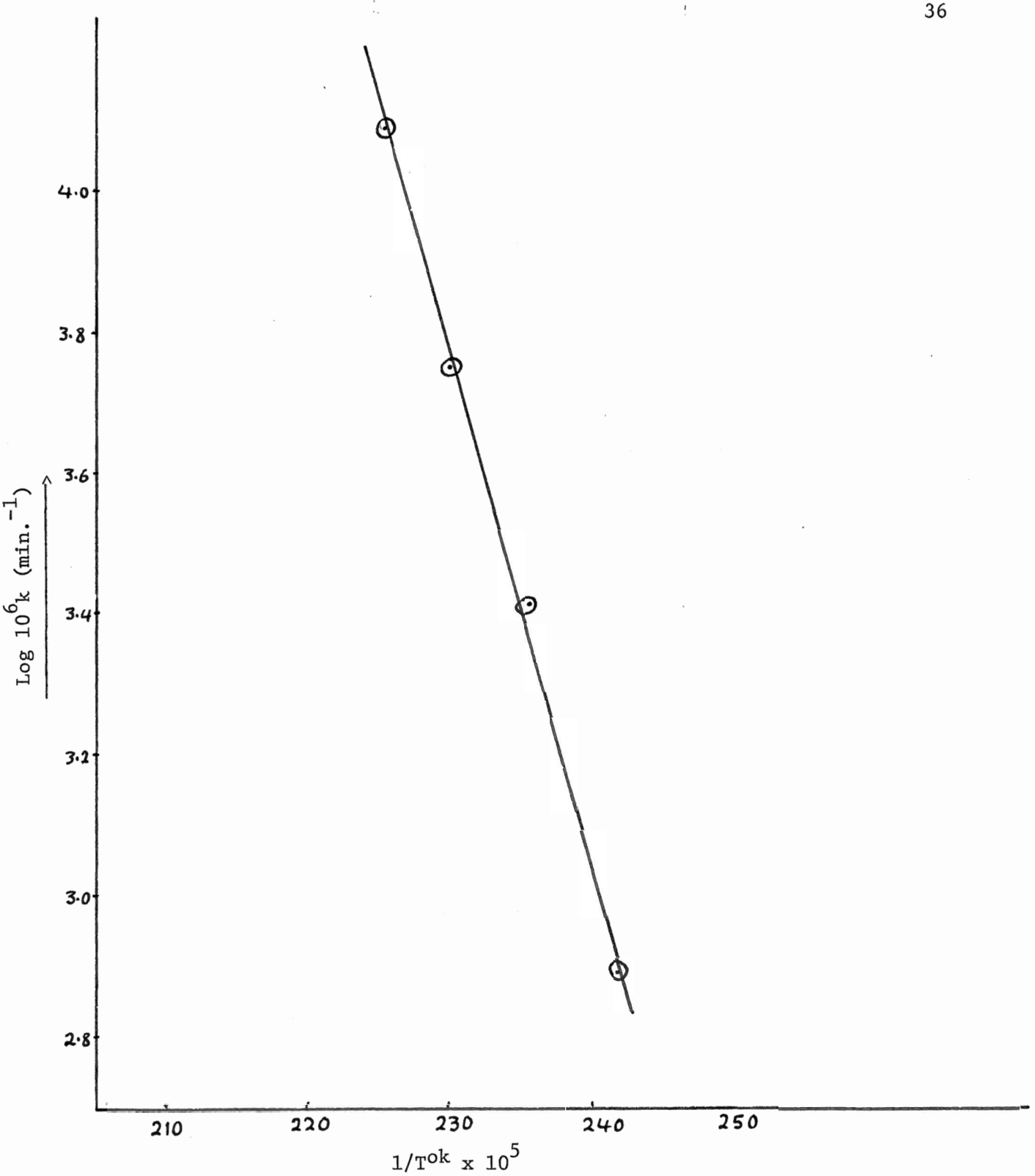
[e] Rate of radical formation at 150°C.

[f] Log frequency factor for overall reaction.

[g] Arrhenius energy of activation.

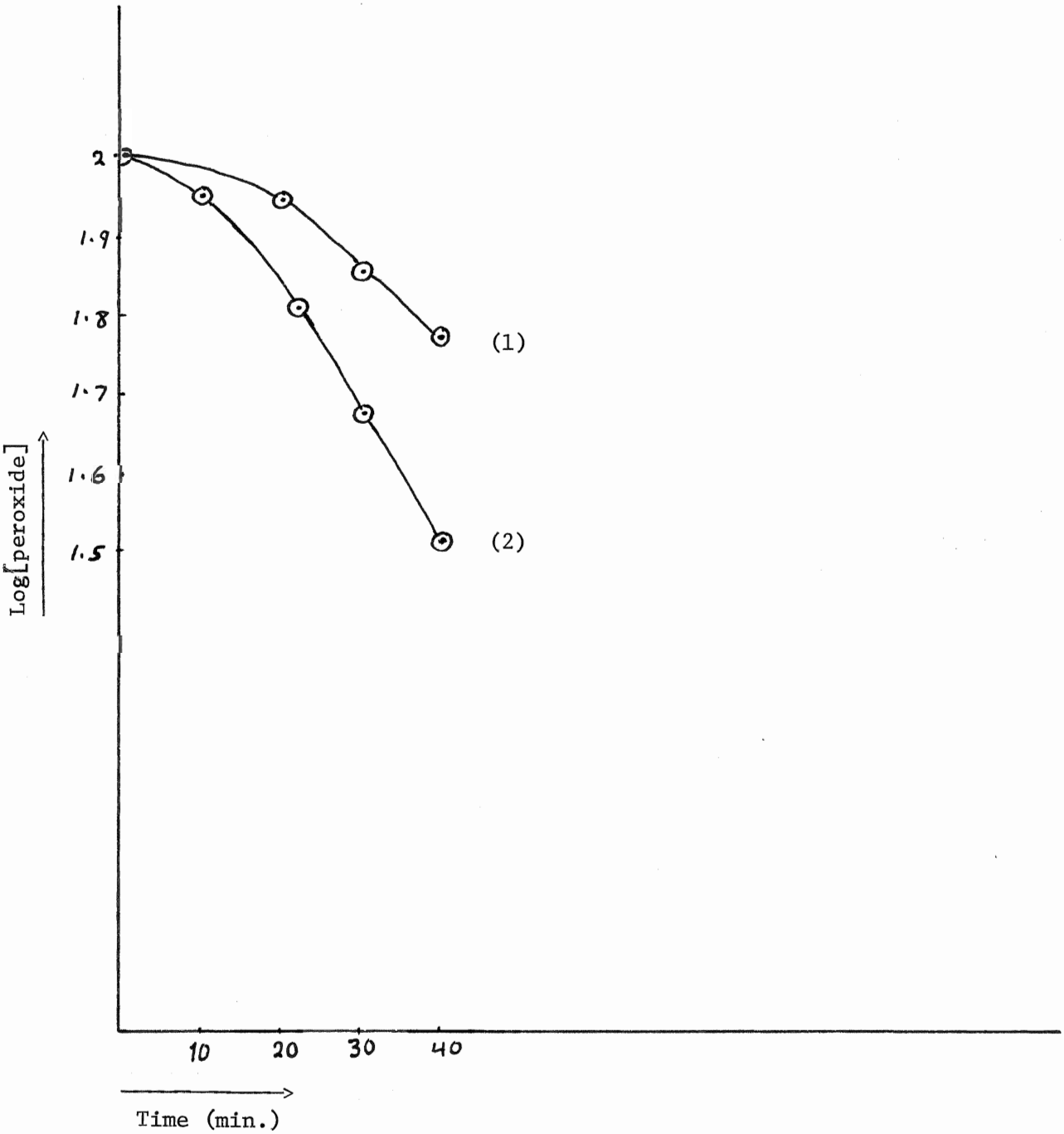
Correlation co-efficient = 0.996

Note: k_H and k_r calculation based on that, not more than 1% hydrogen was produced at 150°C.



Arrhenius energy of activation for decomposition of 1,2-dioxane in tert-butylbenzene-

(Figure 10)



First order plots for the decomposition of 1,2-dioxane in MeOH at 140°C

(1) Initial concentration of .117 mole/1.

(2) Initial concentration of .2186 mole/1.

Table 6

Products of decomposition of isopropyl peroxide
in toluene, isopropyl alcohol, methanol and water

Solvent	Conc. [M][a]	CH_3CHO[b] (%)	$(CH_3)_2CO$[b] (%)	$(CH_3)_2CHOH$[b] (%)	CO[b] (%)	CH_4[b] (%)	H_2[c] (%)
ϕCH_3	.1615	5.37	20.8	68.3	5.23	12.0	7.49
$(CH_3)_2CHOH$	.1524	1.11	50.6	-	0.61	4.23	8.4
MeOH	.1419	6.33	41.6	46.6	-	9.4	30.5
HOH	6.6×10^{-5}	34.9	52.9	12.2	35.9	52.4	41.5

[a] Initial concentration of i-pr_2O_2 in mole/l

[b] % yield based on decomposition peroxide, assuming 1 mole peroxide gives 2 moles of products.

[c] % yield based on decomposition peroxide, assuming 1 mole peroxide gives 1 mole of products.

Note: % yield of bibenzyl for decomposition of isopropyl peroxide in toluene was 51%, based on decomposed peroxide, assuming 1 mole peroxide gives 1 mole of bibenzyl.

Table 7

% Yield of H_2 in ϕCH_3, MeOH, $(CH_3)_2CHOH$ and H_2O at 130-150°C

Temp. °C	Conc. [M][a]	Solvent	"Z"[b] Kcal/mole	H_2[c] (%)
130	.1615	ϕCH_3	60.1	9.0
130	.1615	ϕCH_3	60.1	8.5
130	.1446	MeOH	83.6	33.3
130	5.8×10^{-5}	HOH	94.6	48.1
140	.1615	ϕCH_3	60.1	7.49
140	.1615	ϕCH_3	60.1	7.49
140	.1524	$(CH_3)_2CHOH$	75.9	8.40
140	.1419	MeOH	83.6	30.5
140	6.6×10^{-5}	HOH	94.6	44.4
140	6.6×10^{-5}	HOH	94.6	38.5
150	.1615	ϕCH_3	60.1	5.6
150	.1446	MeOH	83.6	22.1

[a] Initial concentration of i-pr_2o_2 in mole/1.

[b] Kosomer parameters for solvent polarity.

[c] % yield of hydrogen based on decomposed peroxide, assuming 1 mole peroxide gives 1 mole of H_2.

Table 8

Comparison of the rate constants
in various solvents

Solvent	"Z"[a] Kcal/mole	Temp. °C	H_2[b] (%)	k_d 10^{6}[c] sec^{-1}	k_r x 10^{6}[d] sec^{-1}	k_H x 10^{6}[e] sec^{-1}
ϕCH_3	60.1	140	7.5	67.6	62.6	5.0
$(CH_3)_2CHOH$	76.2	140	8.4	339.1	310.6	28.5
MeOH	83.6	140	30.5	219.8	152.6	67.2
HOH	94.6	140	41.5	715.8	419.0	296.6

[a] Kosomer parameters for solvent polarity.

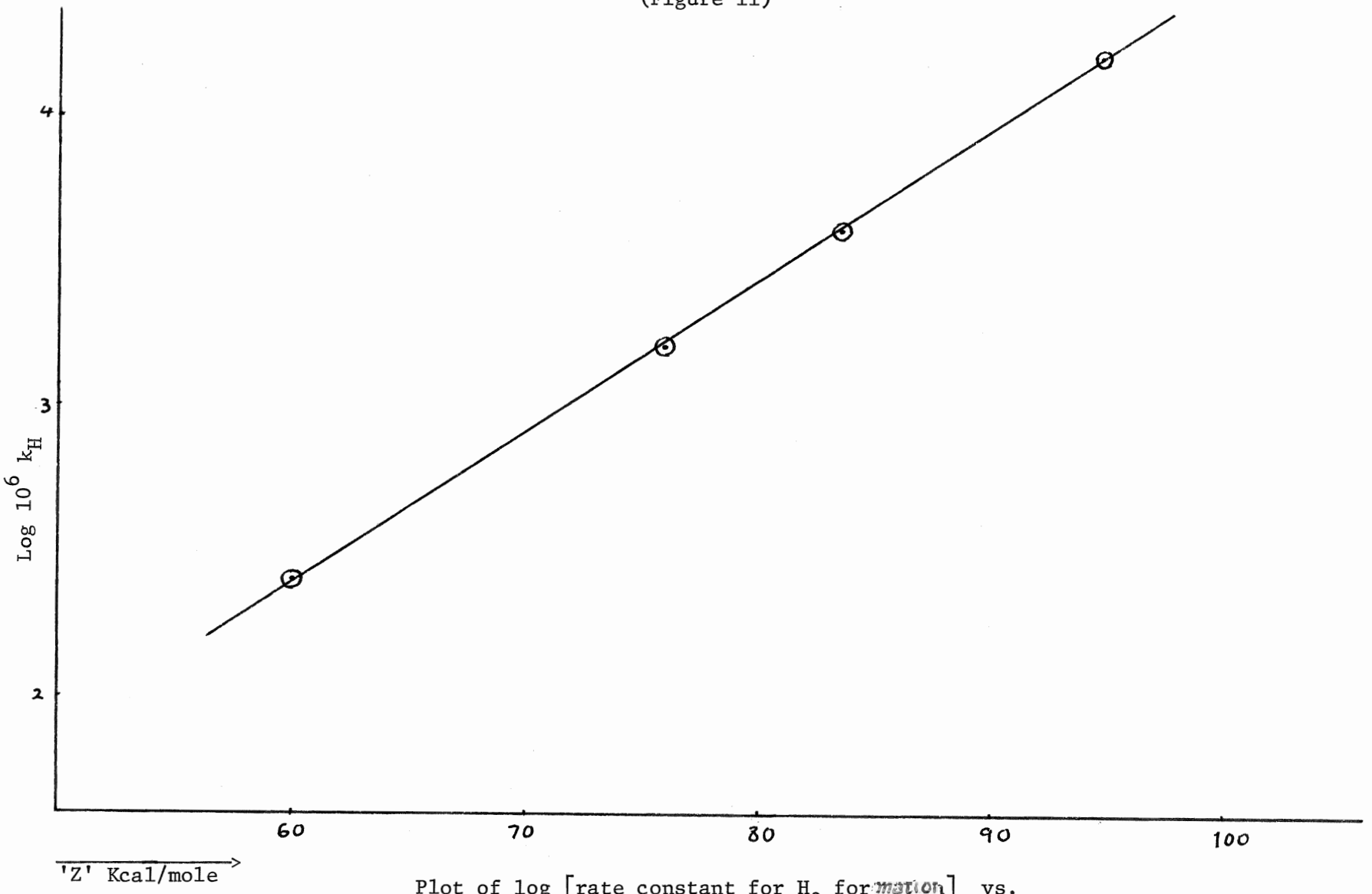
[b] % yield of H_2 based on decomposed peroxide, assuming 1 mole peroxide gives 1 mole H_2.

[c] Overall rate constants.

[d] First order rate for radical formation.

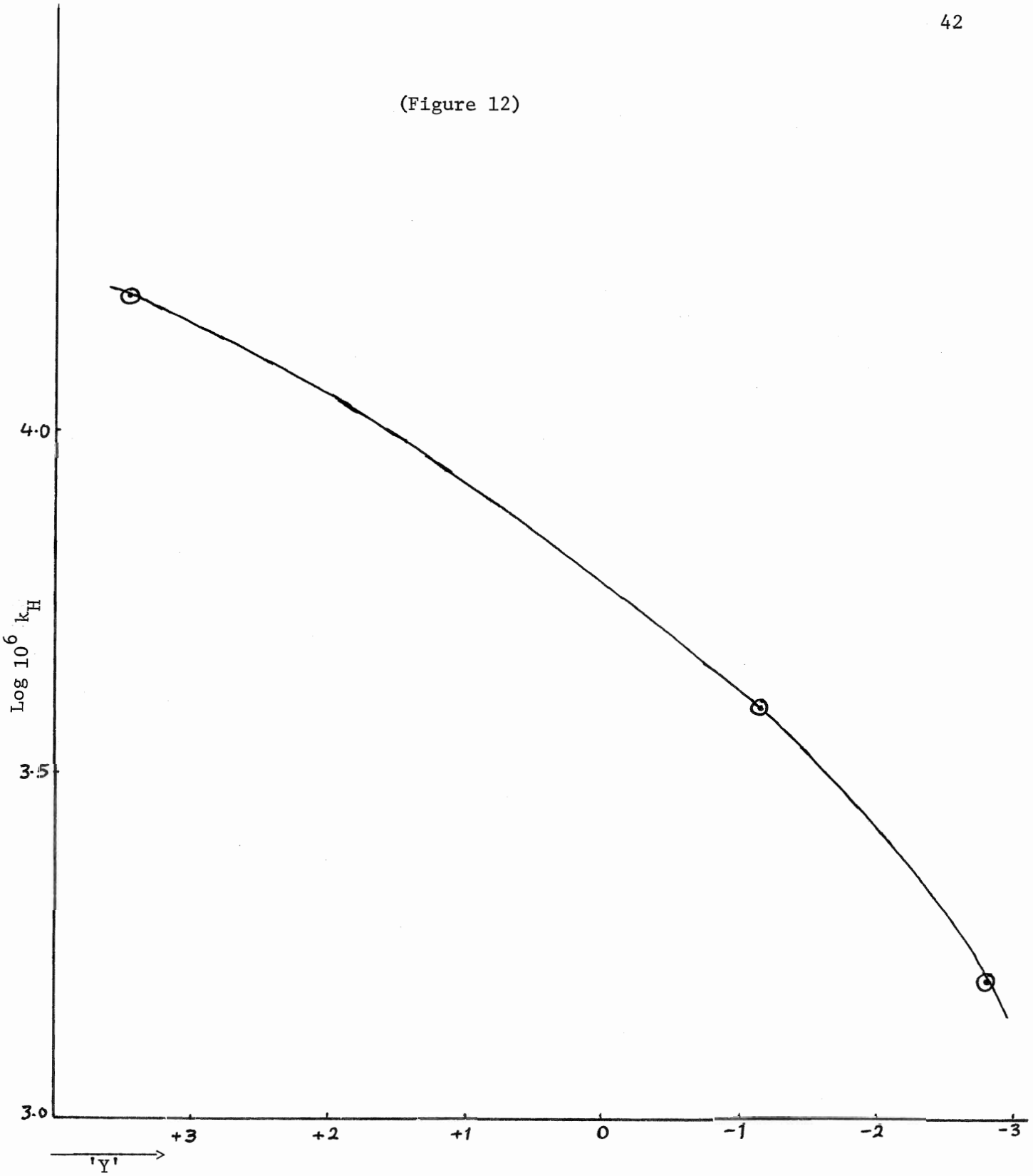
[e] First order rate for hydrogen formation.

(Figure 11)



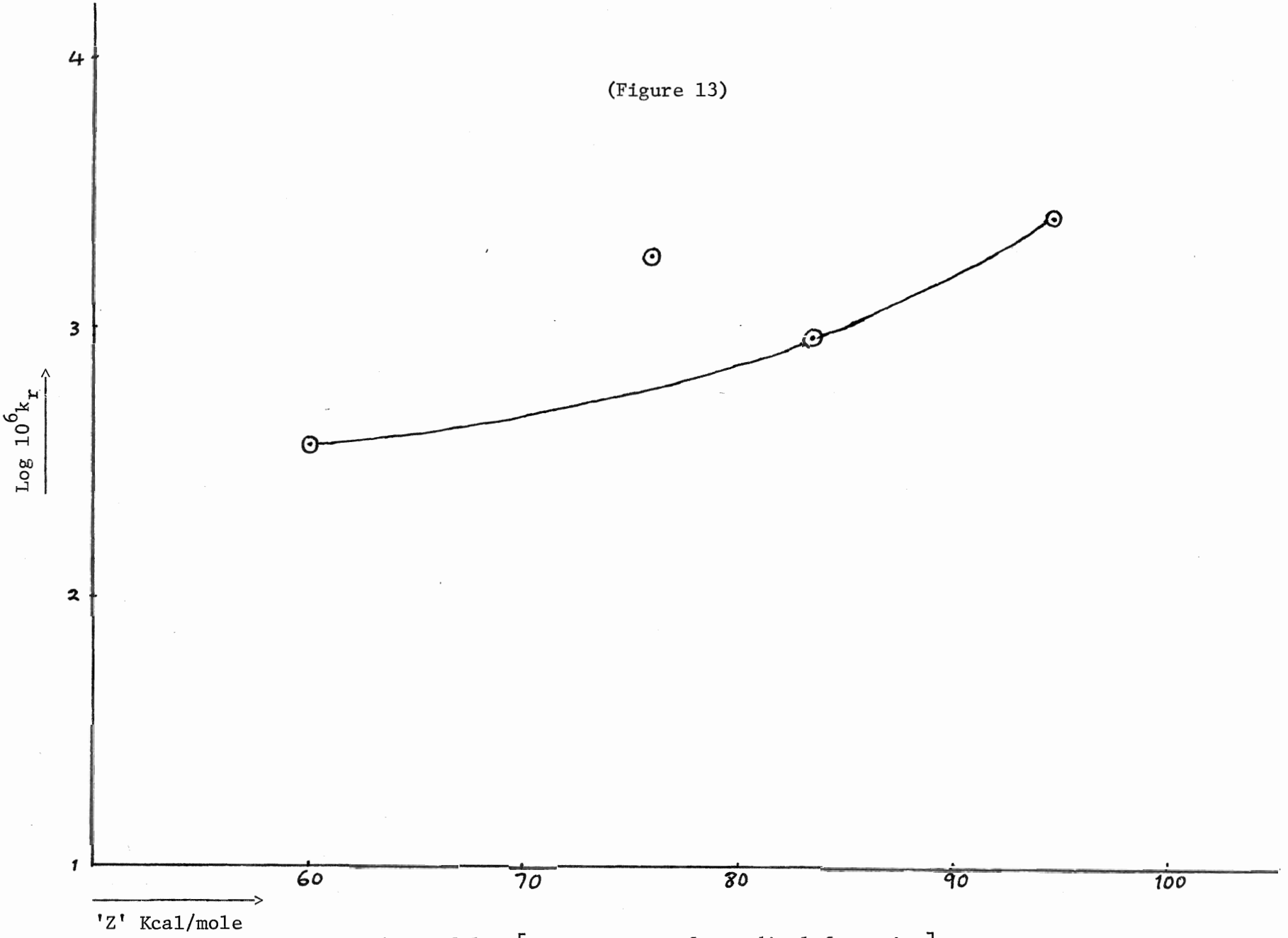
Plot of log [rate constant for H_2 formation] vs.
Kosower parameters 'Z' for solvent polarity

(Figure 12)



Plot of log [rate constant for H_2 formation] vs. Winstein-Grunwald Y-value, parameters for solvent polarity

(Figure 13)



Plot of log [rate constant for radical formation] vs. Kosower parameters 'Z' for solvent polarity

Table 9

Arrhenius parameters. Decomposition of isopropyl peroxide

in Toluene at (130-150)

Conc. [M][a]	Temp. °C	$k_d \times 10^{6b}$ sec^{-1}	$k_H \times 10^{6c}$ sec^{-1}	$k_r \times 10^{6d}$ sec^{-1}	E_d[e] Kcal/mole	E_H[f] Kcal/mole	E_r[g] Kcal/mole	$\log_d A$[h] sec^{-1}	$\log_H A$[i] sec^{-1}	$\log_r A$[j] sec^{-1}
.1583 .0969	130	18.57	1.625	16.949						
.1196 .0875	140	67.	5.01	61.98	39.1	32.1	39.6	16.5	11.63	16.7
.1196 .0909	150	197.5	11.09	186.4						

[a] Initial concentration of i-pr_2o_2 in mole/l.

[b] Overall rate constant.

[c] Rate of H_2 formation.

[d] Rate of free radical formation.

[e] Overall activation energy.

[f] Activation energy for homolysis.

[h] Log frequency factor for overall reaction.

[i] Log frequency factor for hydrogen formation.

[j] Log frequency factor for homolysis.

Table 10

Arrhenius parameters, Decomposition of isopropyl peroxide in MeOH at (130-150)°C

Conc. [M][a]	Temp.	$k_d \times 10^{6}$[b] sec^{-1}	$k_H \times 10^{6}$[c] sec^{-1}	$k_r \times 10^{6}$[d] sec^{-1}	E_d[e] Kcal/mole	E_H[f] Kcal/mole	E_r[g] Kcal/mole	$\log_d A$[h] sec^{-1}	$\log_H A$[i] sec^{-1}	$\log_r A$[j] sec^{-1}
.1419	130	127.6	42.48	85.1						
.1419	140	219.8	67.16	152.6	23.08	17.16	26.3	8.60	5	10.15
.1419	150	533	117.75	415.2						

[a] Initial concentration of $i\text{-}pr_2O_2$ mole/1.

[b] Overall rate constant.

[c] Rate of H_2 formation.

[d] Rate of free radical formation.

[e] Overall activation energy.

[f] Activation energy for hydrogen formation.

[g] Activation energy for homolysis.

[h] Log frequency factor for overall reaction.

[i] Log frequency factor for hydrogen formation.

[j] Log frequency factor for homolysis.

Table 11

Comparison of the rate constants in H_2O and i-PrOH

Solvent	"Z"[a] Kcal/mole	Conc.[M][b]	$k_d \times 10^{6}$ [c] sec^{-1}	$K_r \times 10^{6}$ [d] sec^{-1}	$k_H \times 10^{6}$ [e] sec^{-1}
i-PrOH	76.2	.1524	339.1	310.6	28.5
H_2O	94.6	6.6×10^{-5}	715.8	419.0	296.6

[a] Kosomer parameters for solvent polarity.

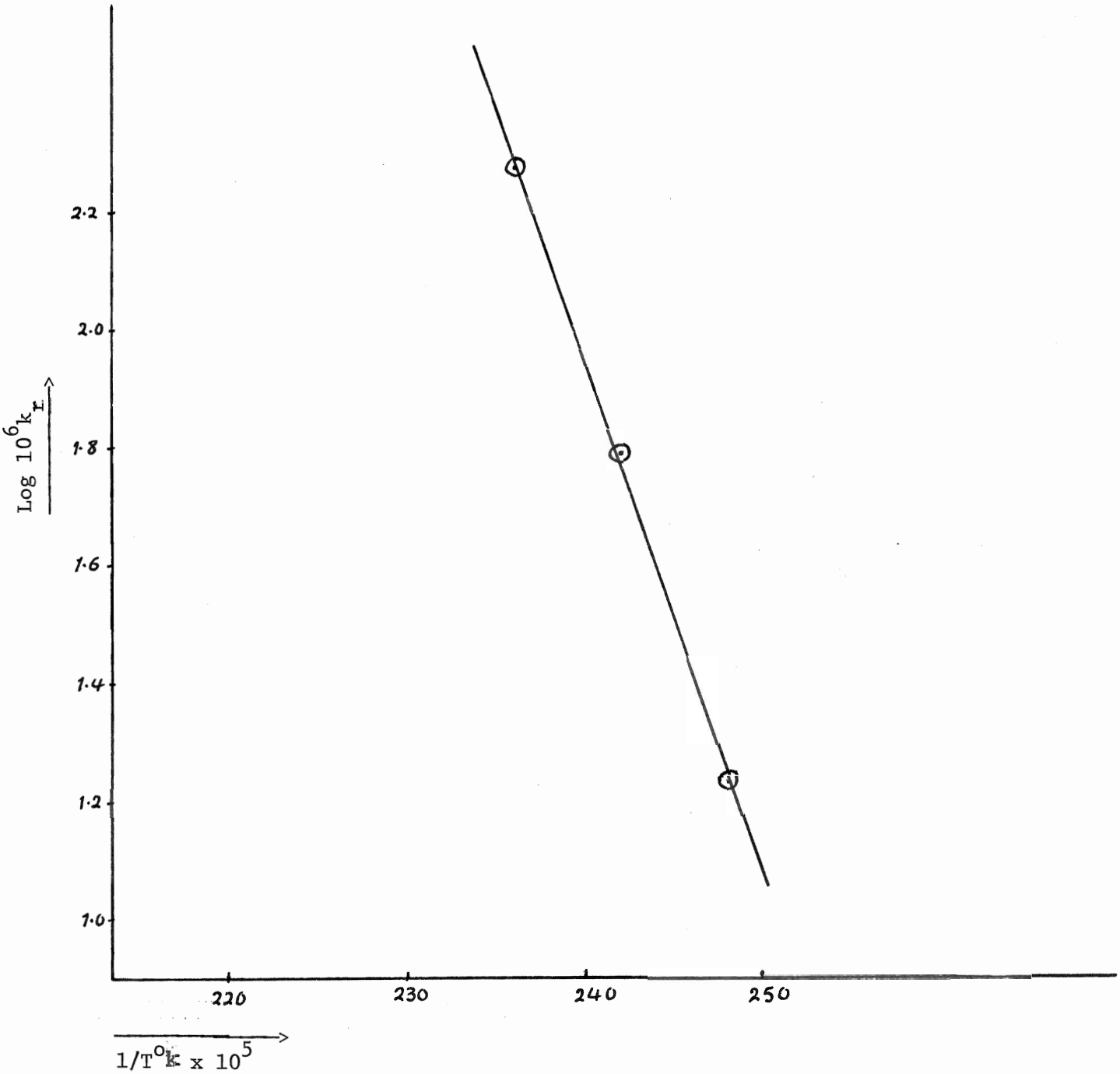
[b] Initial concentration of i-pr_2o_2 in mole/l.

[c] Overall rate constant.

[d] First order rate for radical formation.

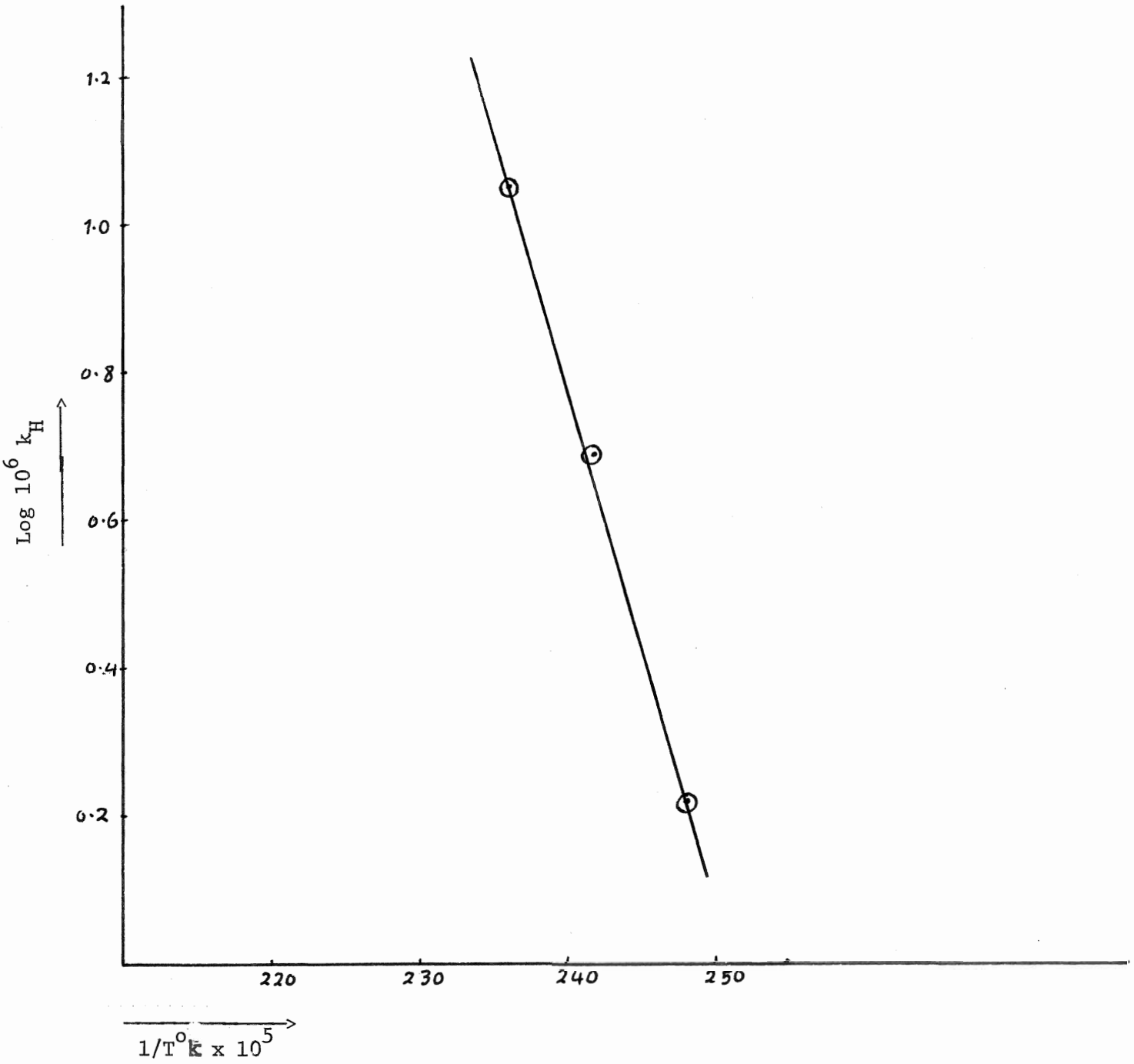
[e] First order rate for hydrogen formation.

(Figure 14)



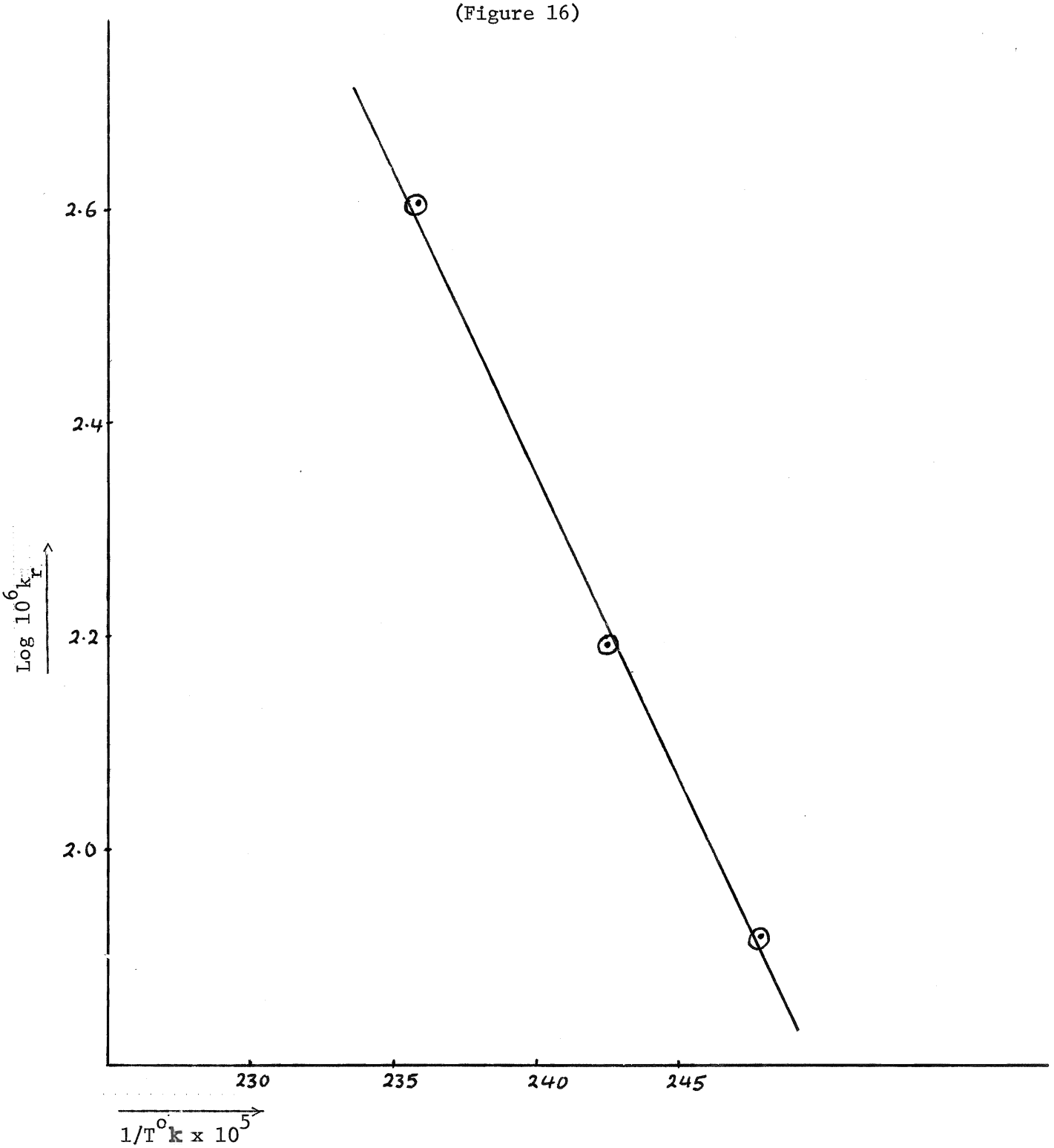
Arrhenius energy of activation for homolysis in decomposition of i-pr_2o_2 in toluene

(Figure 15)



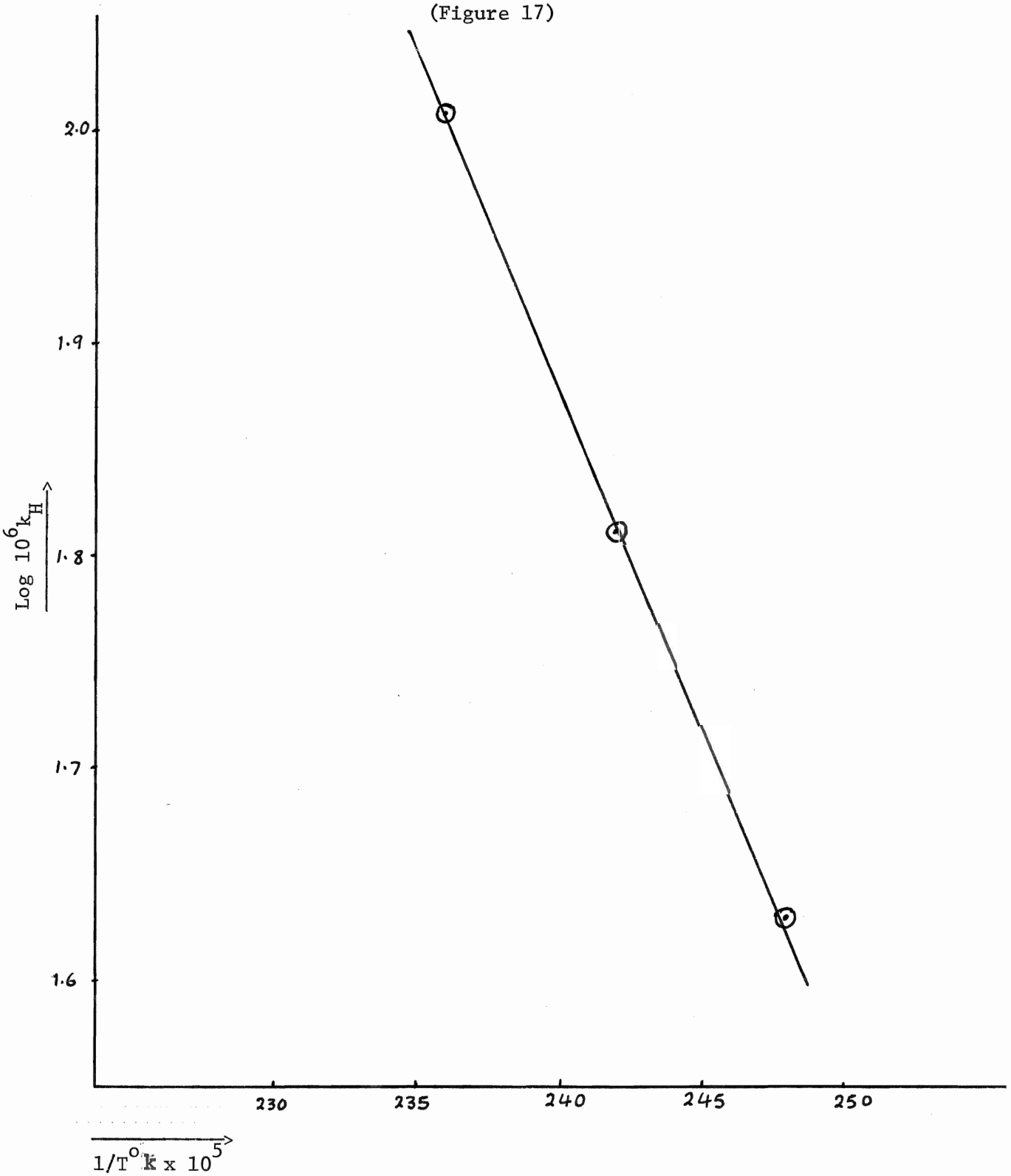
Arrhenius energy of activation for hydrogen formation in decomposition of i-$pr_2{}^{o}{}_2$ in toluene

(Figure 16)



Arrhenius energy of activation for homolysis in decomposition of i-$pr_2{}^{o}{}_2$ in MeOH

(Figure 17)



Arrhenius energy of activation for hydrogen formation in decomposition of i-$pr_2{}^{o}{}_2$ in MeOH

5. Discussion

Interpretation of the results of thermal decompositions of isopropyl peroxide and 1,2 dioxane in a variety of solvents involves a number of general considerations. That is; how do rates for and products from O-O homolysis compare to other measured values for cyclic and acyclic peroxides?; how important is radical induced decomposition and to what extent is this a function of solvent?; what is known about effects of solvent polarity on rates of O-O homolysis or on the rates of the hydrogen forming reaction?; what parameters should be used to quantify polar effects?; should the accelerating effect of polar solvents be ascribed to a polar transition state or to effects on conformation?

Also to be considered is the fact that three of the five solvents used in this work are both protic and reasonably nucleophilic. Nucleophilic displacement on $-\overset{\backslash}{\underset{/}{C}}-O_2R$ has not been observed in decomposition of t-butyl peroxide (see below) and apparently is not a factor in the decomposition of isopropyl peroxide for the same, fairly obvious reasons. For 1,2-dioxane, however, the situation is less clear. The foregoing, it is hoped, will serve as a guide to the following discussion.

5.1 Thermal decomposition of acyclic alkyl peroxides

Rates of thermal decomposition of alkyl peroxides have been mainly studied in the gas phase. Activation energies obtained from these studies suggests that the O-O bond strength is not greatly affected by the variations of the alkyl groups.

Table 12

Activation energies and A factors for thermal decomposition of alkyl peroxides

Peroxide	Ea Kcal/mole	'A' Sec^{-1}	Reference
Me_2O_2 (gas phase)	36.9	4.1×10^{15}	26
Me_2O_2 (gas phase)	35.2 ± 2.5	1.6×10^{15}	27
Et_2O_2 (gas phase)	37.3	3×10^{15}	28
Pr_2O_2 (gas phase)	36.5	2.5×10^{15}	29
i-pr_2O_2 (gas phase)	37.1	$10^{15.4}$	28
t-Bu_2O_2 (gas phase)	39.1	3.2×10^{16}	30
t-Bu_2O_2 (gas phase)	36	4×10^{14}	31
t-Bu_2O_2 (liquid phase in cumene)	37.5	1.6×10^{16}	32
Sec-Bu_2O_2 (liquid phase in toluene)	36.7 ± 1.0	10^{15}	7(a)
$(PhCMe_2O)_2$	34.5	4.3×10^{14}	33
$(Ph_2CHO)_2$ (liquid phase in toluene)	28	$10^{11.6}$	7(b)
$Ph_2\overset{H}{\underset{|}{C}}$-O-O-t-Bu (liquid phase in toluene)	38.6	$10^{16.7}$	7(b)

The activation energy for thermal decomposition of isopropyl peroxide to free radicals (k_r) in toluene we found to be 39.1 Kcal/mole (Table 2). This is in good agreement with the results shown in Table 12, indicating the oxygen-oxygen bond rupture is the main mechanism in operation. The validity of first order kinetics obtained from decomposition of isopropyl

peroxide in toluene (Figure 3) and interpretation of the results can be further substantiated by showing that free radical induced decomposition was not a contributing factor.

5.2 Induced decomposition

The kinetics of decomposition of t-butyl peroxide have been studied both in gas and liquid phases. In the gas phase (30) the rate of decomposition was found to be first order in peroxide, the rate determining step being the homolytic rupture of the O-O bond yielding two t-butoxy radicals. The t-butoxy radicals can decompose to form methyl radicals and acetone;

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO^{\cdot} \qquad (5.2.1)$$

$$(CH_3)_3CO^{\cdot} \longrightarrow CH_3COCH_3 + CH_3^{\cdot} \qquad (5.2.2)$$

$$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow C_2H_6 \qquad (5.2.3)$$

In solution t-butoxy radical abstracts hydrogen from solvent to form t-BuOH,

$$(CH_3)_3CO^{\cdot} + SH \longrightarrow (CH_3)_3COH + S^{\cdot} \qquad (5.2.4)$$

The subsequent reaction will be the combination of two solvent radicals,

$$S^{\cdot} + S^{\cdot} \longrightarrow S - S \qquad (5.2.5)$$

Raley and co-workers (32) have shown that decomposition of this peroxide in cumene, t-butylbenzene and tri-n-butylamine is first order and occurs at the same rate as in the gas phase. They concluded that there is no induced decomposition in these solvents. However, there are instances of induced decomposition of this peroxide. E. R. Bell and co-workers (34) have shown the thermal decomposition of the neat liquid peroxide is faster than

that observed for decomposition in solution or in the gas phase. Their explanation for induced decomposition was based largely on the appearance of isobutylene oxide as a reaction product, produced in the following way.

$$(CH_3)_3CO^{\cdot} + (CH_3)_3COOC(CH_3)_3 \longrightarrow (CH_3)_3COH + {}^{\cdot}CH_2C(CH_3)_2\,OOC(CH_3)_3 \qquad (5.2.6)$$

The new radical decomposes into isobutylene oxide and the chain carrying t-butyl radical. The yield of isobutylene oxide was 35%

$$^{\cdot}CH_2C(CH_3)_2OOC(CH_3)_3 \longrightarrow CH_2\text{-}C(CH_3)_2 \text{ (epoxide O)} + (CH_3)_3CO^{\cdot} \qquad (5.2.7)$$

In the gas phase (35) only 3% of isobutylene oxide is formed. Considering the structure of isopropyl peroxide one would expect that induced decomposition should be easier.

$$R^{\cdot}(RO^{\cdot}) + Me\text{-}\overset{H}{\underset{Me}{C}}\text{-}O\text{-}O\text{-}\overset{H}{\underset{Me}{C}}\text{-}Me \longrightarrow Me\text{-}\overset{\cdot}{\underset{Me}{C}}\text{-}O\text{-}O\text{-}\overset{H}{\underset{Me}{C}}\text{-}Me + RH\ (ROH) \qquad (5.2.8)$$

$$Me\text{-}\overset{\cdot}{\underset{Me}{C}}\text{-}O\text{-}O\text{-}\overset{H}{\underset{Me}{C}}\text{-}Me \longrightarrow Me\text{-}\underset{Me}{C}{=}O + {}^{\cdot}O\text{-}\overset{H}{\underset{Me}{C}}\text{-}Me \qquad (5.2.9)$$

However Pryor and co-workers (23) have shown that the rate constants for chain transfer between polystyryl radicals and alkyl peroxides are about the same for n-butyl, i-propyl, sec-butyl and tert-butyl peroxides.

Table 13

Chain transfer constant for peroxides in polymerization of styrene (23)

	60°C	80°C
n-butyl peroxide[a]	7.6×10^{-4} mole-sec^{-1}	9.4×10^{-4} mole-sec^{-1}
i-propyl peroxide[b]	3×10^{-4} "	15×10^{-4} "
sec-butyl peroxide[b]	4×10^{-4} "	21×10^{-4} "
tert-butyl peroxide[b]	6×10^{-4} "	22×10^{-4} "

[a] in 50-50 styrene-dioxane.

[b] in 50-50 styrene-benzene.

From this table it is evident that primary and secondary peroxides are not more easily attacked by free polystyryl radicals than tert-butyl peroxide is. Generalizing from this data is dangerous, of course. However, Hiatt and Szilagyi (7a) showed that sec-butyl peroxide was not significantly attacked by benzyl radicals in toluene solution at 100-140°C. Induced decomposition can be checked by the following tests:

5.2.1. Kinetic evidence

Decomposition of peroxides which are complicated by induced decomposition frequently exhibit 1 + 3/2 order kinetics

$$-\frac{d[P]}{dt} = k[P] + k_1[P]^{3/2}$$

Such dependence often will not show up in first order plots, but will show as a change in the observed rate constant if the initial concentration

of peroxide is changed. Our results in table 2 shows changing the initial concentration has very little affect on the rate constant. Also, observed activation energies and 'A' factors tend to be lower than normal if there is much induced decomposition. The activation energy of 39.1 Kcal/mole and the 'A' factor of $10^{16.5}$ sec^{-1} obtained for i-pr_2o_2 in toluene again does not agree with significant induced decomposition.

5.2.2. Products of decomposition

Products of decompposition can be indicative of induced decomposition or its absence. As mentioned earlier the formation of isobutylene oxide in decompositions of t-butyl peroxide is evidence for induced decomposition in a positive factor. More obliquely, high yields of solvent dimers indicate its absence, since radical induced decomposition destroys peroxide with no net increase in radical concentration.

$R^{\cdot}(RO^{\cdot})$ + peroxide ⟶ $'R^{\cdot}('RO^{\cdot})$ + non-radical products

For i-pr_2o_2 in toluene (Table 6), the yield of bibenzyl is relatively high, showing that much of the peroxide must have been decomposed to free radicals.

5.2.3. Radical traps and inhibitors

Many cases are known where addition of radical traps either decrease the rate of decomposition, alter the kinetic order, or raise the apparent activation energy. Examples include the thermal decomposition of benzoyl peroxide in dioxane which has kinetic order greater than 1. With the addition of inhibitors like iodine or styrene the kinetics are reduced to first order (36). The activation energy for the decomposition of ethyl peroxide was once thought to be extraordinarily low (37). It was raised to a respectable value by the addition of nitric oxide to the medium (28). The nitric oxide apparently trapped free radicals responsible for induced

decomposition. No radical trap tests have been done in our work, since other evidence against induced decomposition in toluene solution seemed convincing.

5.2.4 Radical induced decomposition in other solvents

Hydrogen atom abstraction from peroxide is the conventional mode of induced decomposition. Hydrogen atom addition to peroxide, however, has been proposed by Huyser and co-workers (38,39) to account for accelerated rates of decomposition of t-butylperoxide in alcohol (38) or amine (39) solvents.

In these cases the requirement for solvent-derived radicals to induce the decomposition of tert-butyl peroxide was that radical site be an atom bonded to either a hydrogen group or to an amino group having at least one hydrogen bonded to nitrogen. Although tertiary amines (40) as well as ethers (41) increased the decomposition rates of diacyl peroxides, tri-n-butylamine (39) did not have any appreciable effect on the rate of decomposition of tert-butyl peroxide. In Table 14 and 15 the rates of decomposition of tert-butyl peroxide in amines and alcohols are listed.

Table 14 Ref(39)

First order rate data for the decomposition of peroxide in amines at 125°C

Solvent	Initial mole ratio of solvent: peroxide	$k \times 10^5$ sec^{-1}
Toluene	9.07	1.62
N-Methylpiperidine	9.00	1.54
γ-collidine	10.8	1.64
Piperidine	10.2	3.49
N-Ethylcyclohexylamine	8.92	4.01
Cyclohexylamine	9.01	5.50

Table 15 Ref(38)

First order rate constant for decomposition of tert-butyl peroxide in alcohols at 125°C

Solvent	Mole ratio of solvent: peroxide	$k \times 10^5$ sec^{-1}
Cyclohexane	9.02	1.4
Cyclohexanol	8.95	2.4
1-Propanol	10.88	2.8
Norborneol	8.94	4.4
2-Butanol	8.87	4.8 ± 0.2
2-Octanol	8.88	5.5
Benzhydrol	4.36	8.7

Analysis of kinetic results indicated that decomposition of the peroxide in primary and secondary alcohols and amines involve the peroxide in some reaction other than the unimolecular oxygen-oxygen rupture. From reaction products it is obvious that attack is at the oxygen-oxygen, since acetone and t-butyl alcohol are produced. (Decomposition in primary and secondary amines will produce related imine and t-butyl alcohol). They proposed a mechanism which is identical for both in alcohols and amines.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO^{\cdot} \qquad (5.2.10)$$

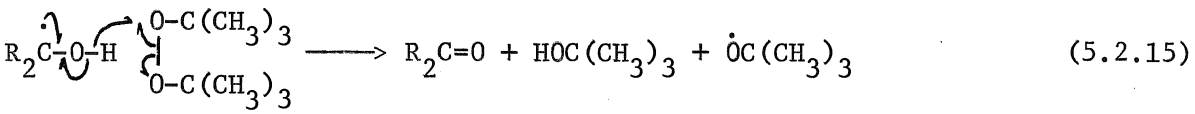
$$(CH_3)_3CO^{\cdot} \xrightarrow{k_2} CH_3COCH_3 + CH_3^{\cdot} \qquad (5.2.11)$$

$$(CH_3)_3CO^{\cdot} \text{ or } CH_3^{\cdot} + R_2CHOH \xrightarrow{k_3} (CH_3)_3COH \text{ or } CH_4 + R_2\dot{C}OH \qquad (5.2.12)$$

$$R_2\dot{C}OH + (CH_3)_3COO(CH_3)_3 \xrightarrow{k_4} R_2C{=}O + (CH_3)_3COH + {}^{\cdot}OC(CH_3)_3 \qquad (5.2.13)$$

$$R_2\dot{C}OH + (CH_3)_3CO^{\cdot} \xrightarrow{k_5} R_2C{=}O + (CH_3)_3COH \qquad (5.2.14)$$

The two step mechanism in equation (5.2.13) involving the attack of an α-hydroxy alkyl radical to the oxygen-oxygen linkage of tert-butyl peroxide which produces hemiketal which in turn could decompose to the observed ketone and t-butyl alcohol was rejected since there was detectable α-t-butonytetrahydropyran when decomposition was conducted in tetrahydropyran. The most satisfactory mechanism which involves transfer of a hydrogen atom from the hydroxy function of the radical is shown below.



(5.2.15)

This mechanism is energetically favored also, since bond energy formation of Dc=o is ∿ 150 Kcal/mole where as breaking of Dc-o is about 77 Kcal/mole and Do-o is ∿ 37 Kcal/mole, thus overall reaction is exothermic to the extent of about 36 Kcal/mole. Huyser and co-workers derived a rate expression for disappearance of peroxide in alcohol by applying steady state approximation and assuming that the termination step is only reaction (5.2.14)

$$-\frac{d[per]}{dt} = [k_4 + (\frac{k_4}{k_1} \pm \frac{k_1}{2k_4}\sqrt{\frac{1}{4} + \frac{2k_3k_4[R_2CHOH]}{k_1k_5}})][per] \qquad (5.2.16)$$

(where "per" = $t\text{-}Bu_2O_2$)

This expression shows that the rate of reaction depends also on $[R_2CHOH]$, but since the concentration of R_2CHOH is comparatively high $[R_2CHOH]$ does not change appreciably during the course of reaction. Also this expression shows that the rate depends on particular alcohol used since k_3, k_4 and k_5 are involved in the constant term.

What Huyser, et al, did not do was to change the initial peroxide concentration. Thus, while the mechanism of H atom transfer seems quite

acceptable, the kinetic development is obviously designed to achieve a result that is not experimentally proved.

5.3 Effects of solvent polarity.

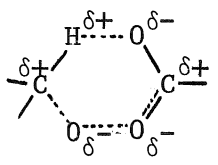
While the chemical nature of the solvent may influence the importance of radical-induced decomposition of peroxides, gross polar effects may be important in the H_2 forming reaction (Type 3) and in the 0-0 homolysis (Type 1).

Previously these have been studied in terms of competition between Type 1 and Type 3 reactions in the vapor phase vs. solution and in solution when solvent polarity is varied the effect of solvent polarity on simple 0-0 homolysis has also been investigated. These findings will be considered in turn.

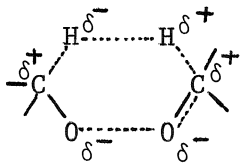
5.3.1. Vapor phase vs. solution on Type 3 vs. Type 1

Liquid and gas phase decompositions of some primary and secondary alkyl peresters by R. Hiatt et al. (8) showed different mechanisms. In liquid phase reactions of Type 1 and 3 compete where as in gas phase simple homolysis of the 0-0 bond is the main path. R. Hiatt and Szilagyi (7a) investigated the liquid and gas phase thermal decompositions of sec-butyl peroxide. In the gas phase, the H_2 yield was less than 1%, whereas it was 25-30% in the liquid phase. From these observations it seemed quite possible that the solvent caused stabilization of a transition state conformation which would favor the concerted mechanism of Tupe 3 in solution, while in the gas phase, some other conformation might predominate. R. Hiatt et al. (8) also suggested the alternative possibility of ionic contribution to the transition state and postulated that the six-centered transition state possessed sufficient ionic character, (as shown in formulae I and II) to be stabilized by solvent interaction, thereby the concerted pathway becomes important. In the gas phase without solvent

stabilization homolysis becomes the preferred reaction course.



I (Type 3b)



II (Type 3c)

In this work isopropyl peroxide was chosen to test the importance of solvent polarity in decomposition of Type 3c and this has been demonstrated by the increased rate of H_2 formation as the polarity of the solvents in which peroxide was decomposed was increased from toluene to $(CH_3)_2CHOH$, MeOH and H_2O.

5.3.2. Values which correlate the rates of reactions to the solvents polarity.

In discussion of the effect of the solvent on reaction rate it is convenient to distinguish between four types of reactions,

1. Reaction between neutral, nonpolar molecules giving nonpolar activated complexes.
2. Reaction between neutral molecules and ions.
3. Reaction of neutral molecules giving dipolar activated complexes.
4. Reaction between ions.

of these, reaction type 3 will be considered in detail.

Typical examples of relatively nonpolar reactants giving dipolar activated complexes are the Menschutkin reaction (the reaction of an amine with an alkylhalide) and the solvolysis of tertiary alkylhalides.

$$R_3N: + RCH_2\,x \longrightarrow [R_3N^{+\delta}\cdots C(H)(H)(R)\cdots x^{\delta-}] \longrightarrow R_3\overset{+}{N}-CH_2R + x^- \qquad (5.3.1)$$

A list of tables showing the dependence of the rate constants on the dielectric constant of the solvent for different reactions are found in reference 42. These tables and graphs show that the dielectric constant is not a useful value for describing the effect of the solvent on a dipolar species (or an ion) except in certain special cases such as the use of a mixture of two solvents. Also Winstein (43) demonstrated that the dielectric constant, D, is not a quantitative measure of solvent polarity when the range of ionizing power is great.

Another factor (value) which correlates the rate of the reaction to the polarity of the solvent is the so-called 'Y' value proposed by Winstein and Grunwald (44). Winstein prefers this value to be called the ionizing power of the solvent. The Winstein-Grunwald equation, $\log \frac{k}{k_o} = Ym$ gives a satisfactory correlation of the rates of solvolysis of a few tertiary halides and secondary sulfonate esters. The failure of this equation when applied to secondary halides is to be expected since nucleophilic push contribution in solvolysis of secondary halides is important and, not considered in the Grunwald equation. Here agreement is good for solvolyses in various mixtures of the same two solvents. If we take the 'Y' values obtained from the study of the solvolysis of t-butyl chloride in various solvents and mixtures of solvents and plot them against the logarithms of the solvolysis rates for say benzhydryl-chloride in the same solvents, the points are badly scattered.

In this work a new empirical measure of solvent polarity, the 'Z' value is used. Solvent sensitivity of the absorption spectrum of pyridine-1-oxide was previously reported by Ito (45). E. M. Kosower (46) reported that the position of the charge-transfer (c.-t.) absorption band of 1-alkylpridinium iodide complexes is remarkably sensitive to the nature of the

solvent in which it is measured. He suggested that the activation energies in Kcal/mole for this electronic transition be taken as a measurement of solvent polarity and be called 'Z' values. Charge-transfer bands can be measured in solvents in which it is not possible or convenient to obtain a 'Y' value. The use of 'Z' values in connection with kinetic data has been investigated by Kosower (46).

5.3.3. Effect of solvent polarity on decomposition of alkyl peroxides.

Although Hiatt and co-workers in studies of sec-butyl (7a) and diphenyl methyl (7b) peroxides using such solvents as Nujol, toluene, nitrobenzene and acetonitrile, concluded solvent character had no significant effect on the H_2-forming vs. free radical-forming competition, they did not consider the effect of solvent on the individual rate constants.

Previous knowledge concerning the effect of solvent polarity on the rate of peroxide O-O homolysis is limited to tert-butyl peroxide and to the work by Huyser and co-workers (38,39) and later by Huyser and Vanscoy (20) and Walling (21). These authors investigated effect of solvents on decomposition of tert-butyl peroxide in two sets of solvents, solvents which promote induced decomposition (discussed earlier) and solvents which do not promote induced decomposition. In the latter, it was found, for example, that tert-butyl peroxide at 125°C homolyzed 2.5 times faster in acetonitrile than in cyclohexane (20,21). First-order rate constants for homolysis were measured in a number of solvents, and activation parameters were calculated (20).

Table 16 Ref(20)

Activation parameters

Solvent	$\Delta H^{\dagger}$ Kcal/mole	Probable error	$\Delta S^{\dagger}$ eu	Probable error
Acetonitrile	31.0±0.9	0.8	-1.54±0.06	1.99
Acetic acid	33.4±0.5	0.7	4.58±0.08	1.74
t-butyl alcohol	34.3±0.07	0.9	5.89±0.02	2.25
Benzene	35.3±1.1	0.9	7.96±0.32	2.25
Ethylbenzoate	35.5±0.02	0.8	8.42±0.00	2.08
Nitrobenzene	35.6±0.4	0.4	9.04±0.00	0.95
t-Amylalcohol	35.7±1.4	0.8	9.33±0.49	2.15
Tetrahydrofuran	37.1±0.5	0.6	12.3 ±0.2	1.6
Cyclohexane	37.3±1.4	0.7	12.4 ±0.6	1.9
Dimethylaniline	37.6±0.8	0.5	13.6 ±0.4	1.2
Gas phase	38		14	
Triethylamine	40.6±1.2	1.2	20.9 ±0.7	2.9
Cyclohexane	40.8±2.2	2.1	21.1 ±1.4	5.2

Heats of solution of t-butyl peroxide were measured in these solvents and shown to be almost the same, indicating that the differences in activation parameters are due to interaction of the solvents with peroxide in the transition state rather than in the ground state. The solvent effect on the activation parameters can be attributed to three factors.

1. Differences in solvent interactions with the alkoxyl radical-like transition state.
2. Different solvent cavity requirements for the transition state.
3. Different amounts of cage recombination.

t-Butyl peroxide in ground state has more hydrocarbon character and it can be solvated by non-polar solvents, e.g., triethylamine and cyclohexane, as well as by polar solvents. However, the transition state t-butyl peroxide is completely different in that it has more t-butoxyl radical character and possibly some polar characteristics. In any case the oxygens of the peroxide linkage are more exposed to interaction with solvent molecules. Passing from the transition state to the two t-butoxyl radicals in the solvent cage, these may interact with the polar solvent molecules so that cage recombination will be minimized. The low activation parameters in more polar solvents are thus rationalized.

5.4 Solvent effect studies in this work

Decompositions of sec-alkyl peroxides are different from those of t-butyl peroxide. Secondary alkyl peroxides are knwon to decompose by two different pathways, i.e., radical decomposition and a concerted mechanism. Solvent effects on the rate of radical formation (k_r) and on the rate of hydrogen formation (k_H), concerted mechanism, should be considered separately.

5.4.1. Effect of solvent on k_H (rate of hydrogen generation) in decomposition of isopropyl peroxide

The suggested six-centered concerted transition state for decomposition of non-tert alkyl peroxides and its apparent preference for the liquid phase suggesting ionic contributions (8) to this transition state has been investigated by studying the effect on the rate of H_2 generation from decomposition of isopropyl peroxide by a variety of solvents.

Hiatt et al (7a) in their studies of thermal decomposition of sec-butyl peroxide in toluene found an activation energy of 31 Kcal/mole and 'A' factor of 10^{12} for H_2 evolution which they though was not low enough for a concerted mechanism. However, semi-empirical calculations for iso-

propyl peroxide later showed that 10^{12} is about right for an 'A' factor for the concerted reaction (47). Our experimental result for decomposition of isopropyl peroxide in ϕCH_3 is an 'A' factor of $10^{11.6}$, in good agreement with the theoretical value.

The question arises why the concerted pathway is not important in gas phase (no H_2 in the gas phase)? (For thermal decomposition in the gas phase see ref. 28). This question can be answered by the result obtained in this work.

The presumption existed that the postulated six-centered concerted transition state (for H_2 evolution) possessed sufficient ionic character to be stabilized by solvent interaction making that pathway relatively as accessible as homolysis in solution. In the gas phase without solvent stabilization, homolysis would become the preferred reaction course.

To test this idea the yields of H_2 from decomposition of isopropyl peroxide in four different solvents with 'Z' values ranging from 60 Kcal/mole to 94.6 Kcal/mole were measured at 140°C (Table 8). The percentage of H_2 varied from ~7.5% in toluene to ~41% in H_2O. That H_2 yield, itself, may be misleading as shown by resuls of the decomposition in $(CH_3)_2CHOH$. In that solvent the H_2 yield was found to be 8.4%, about the same as found in toluene. But, since the overall rate of decomposition is much higher in $(CH_3)_2CHOH$ (due to radical induced decomposition, as will be shown) than in ϕCH_3 the rate of hydrogen formation (k_H) is significantly higher than in ϕCH_3 (k_H is independent of induced decomposition). Having overall rate of decomposition in four solvents at 140°C, the yield of hydrogen and assuming that $k_d = k_H + k_r$

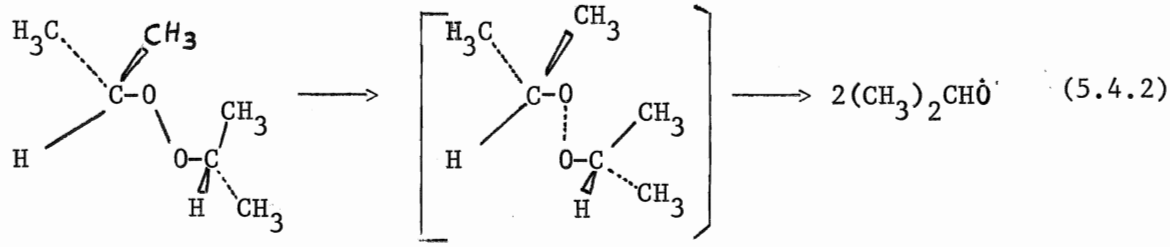
$$\text{i-Pr}_2\text{O}_2 \begin{cases} \xrightarrow{k_H} & H_2 + CH_3\overset{O}{\overset{\|}{C}}\text{-}CH_3 \\ \xrightarrow{k_r} & 2\ \text{i-PrO}\cdot \end{cases} \qquad (5.4.1)$$

The rate constants for hydrogen formation (k_H) in these solvents were found (Table 8). It can be seen that k_H increases with increasing polarity of the solvent. A plot of log k_H vs. 'Z' values for the solvents is perfectly linear (Figure 11). A plot of log k_H vs. "Y" values was also made (Figure 12). It was not linear. However, since many of Kosomer's plots of log[rate constants] for polar reactions vs. "Z" were also non linear, the major importance attached to the linearity of log k_H vs "Z" is aesthetic.

Low activation parameters for this process, E_Ha and $\log_HA$ found from decomposition of isopropyl peroxide in MeOH (Table 10) comparing in ΦCH_3 (Table 9) is inconsistent with the suggested ionic contribution to the six-centered concerted transition state.

5.4.2. Effect of solvent on k_r (Rate of radical formation) in decomposition of isopropyl peroxide

In (Table 8) the rate of radical formation in the decomposition of isopropyl peroxide in different solvents are listed. By increasing the polarity of the solvent the rate of formation of free radical (k_r) has increased. This clearly shows that the interaction of the solvents with peroxide in going from less polar solvent to more polar solvent is more important in the transition state than in the ground state. Peroxide, at the transition state, has i-PrO$^{\cdot}$ character and interactions of peroxide linkage with solvent molecules are more pronounced.



(5.4.2)

The ground state of the peroxide has more hydrocarbon character since the two oxygens of the peroxide linkage are protected by the two i-Pr groups from direct interaction with the solvent. These facts are reflected by the lower activation parameters, $E_r a$ and $\log_r A$ (Table 9, 10) found in MeOH compared to that in ϕCH_3. Decomposition of isopropyl peroxide in isopropyl alcohol is more complicated. Radical induced decomposition is a large factor as can be seen both from the product balance (Table 6) and the kinetic data (Table 8). Induced decomposition of peroxides by secondary alcohols can be represented as follows; (this is a slightly simplified version of the Huyser scheme reproduced earlier.)

$$R'\text{-}O\text{-}O\text{-}R' \xrightarrow{k_1} 2\ R'O^{\cdot} \tag{5.4.3}$$

$$R'O^{\cdot} + R_2CHOH \xrightarrow{k_2} R'OH + R_2\dot{C}OH \tag{5.4.4}$$

$$R_2\dot{C}OH \xrightarrow[+R'OOR']{k_3} R_2C{=}O + R'OH + \dot{O}R' \tag{5.4.5}$$

$$R_2\dot{C}OH + R'O^{\cdot} \xrightarrow{k_4} R_2C{=}O + R'OH \tag{5.4.6}$$

By applying the steady state approximation and assuming that the termination reaction is only reaction (5.4.6) we will find,

$$-\frac{d[P]}{dt} = k_1[P] + k_3[R_2\dot{C}OH][P] \tag{5.4.7}$$

$$2k_1[P] + k_3[R_2\dot{C}OH][P] - k_2[R'O^{\cdot}][R_2CHOH] - k_4[R'O^{\cdot}][R_2\dot{C}OH] = 0 \tag{5.4.8}$$

$$k_2[R'O^{\cdot}][R_2CHOH] - k_3[R_2\dot{C}OH][P] - k_4[R'O^{\cdot}][R_2\dot{C}OH] = 0 \tag{5.4.9}$$

So,

$$k_1[P] = k_4[R_2\dot{C}OH][R'O^{\cdot}] \tag{5.4.10}$$

substitution $[R'O^{\cdot}]$ from (5.4.10) in (5.4.9) gives.

$$\frac{k_1 k_1[P][R_2CHOH]}{k_4[R_2\dot{C}OH]} - k_3[R_2\dot{C}OH][P] - k_1[P] = 0 \tag{5.4.11}$$

or,

$$\frac{k_1 k_2}{k_4}[R_2CHOH] + k_3[R_2\dot{C}OH]^2 + k_1[R_2\dot{C}OH] = 0 \qquad (5.4.12)$$

$$[R_2\dot{C}OH] = \frac{-k_1 \pm \sqrt{k_1^2 + \frac{4k_1k_2k_3}{k_4}[R_2CHOH]}}{2k_3} \qquad (5.4.13)$$

substitution of (5.4.13) in (5.4.7) gives,

$$-\frac{d[P]}{dt} = k_1[P] + [P]\,\frac{-k_1 \pm \sqrt{k_1^2 + \frac{4k_1k_2k_3}{k_4}[R_2CHOH]}}{2} \qquad (5.4.14)$$

$$-\frac{d[P]}{dt} = k_1[P] - \frac{k_1}{2}[P] \pm \left(\sqrt{\frac{1}{4} + \frac{k_2k_3}{k_1k_4}[R_2CHOH]}\right)[P] \qquad (5.4.15)$$

$$-\frac{d[P]}{dt} = \frac{1}{2}k_1[P] \pm \left(\sqrt{\frac{1}{4} + \frac{k_2k_3}{k_1k_4}[R_2CHOH]}\right)[P] \qquad (5.4.16)$$

The higher k_r obtained from the decomposition of isopropyl peroxide in $(CH_3)_2CHOH$ compared to k_r in MeOH is certainly due to induced decomposition in the former solvent. Although the above rate expression shows that the disappearance of the peroxide is dependent on $[R_2CHOH]$, the concentration of alcohol does not change significantly during the reaction, and it can be considered as a constant. Decomposition in MeOH appeared not to be complicated by induced decomposition, since the expected product, $H\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$, produced from the free radical derived from MeOH if there is any induced decomposition, was present only in trace amount, (not measured quantitatively).

The plot of log k_r vs. "A" in the four solvents is illustrated in

The correlation is certainly not linear but it does appear as a smooth curve. The point for isopropyl alcohol again suggests that the rate of disappearance of peroxide in this solvent is much faster than expected, and is ascribed, as we have said, to induced decomposition. (Table 8) shows that k_r does not change very much by changing the polarity (60 Kcal/mole in ϕCH_3 to 94.6 Kcal/mole in H_2O. However, the activation parameters determined from the first order reaction rate constants (given in Table 10 for MeOH and Table 9 for ϕCH_3) show that the solvent apparently does have a marked effect on the decomposition reaction. Examination of these activation parameters shows that a change in Ea ($\Delta H^{\dagger}$ = Ea-nRT) is always accompanied by concurrent change in 'A' factor $\Delta S^{\dagger}$). The linear correlation is known as isokinetic relationship, $\Delta H^{\dagger} = \beta \Delta S^{\dagger}$ where B is isokinetic temperature. A decrease in $\Delta H^{\dagger}$ due to solvent interaction which increases the reaction rate, is accompanied by a decrease in $\Delta S^{\dagger}$ which retards the rate. In this work since ΔS is not calculated this relationship can be seen by comparing Ea, and the 'A' factor.

5.5. Conformational effects

As mentioned earlier, the effect of solvent polarity on k_H could be explained either in terms of a polar transition state, or as a stabilizing effect on the conformation required for the six-centered concerted reaction. While the results of this work do not permit a decision between the two possibilities, the conformational aspect is discussed, both for completeness and as a possible stimulus to further work.

The structure of hydrogen peroxide, the parent member in the peroxide family has been studied in detail (48). The dihedral angle was calculated 90^{o} by including the repulsion of unshared electron pairs and it was suggested by Penny and Sutherland (49) that repulsion between hydrogen atoms would

enlarge this angle to 100°. A dihedral angle was calculated for t-butyl hydroperoxide (ϕ = 100°) and n-butyl-t-butyl peroxide (ϕ = 150°) based on the fixed skew, in general accordance with this angle in hydrogen peroxide. For t-butyl peroxide the dihedral angle is (ϕ = 130°) which has been explained as a steric effect of the two large t-butyl groups. Conformational requirements for three types of decomposition of organic peroxides (see introduction) will be discussed respectively.

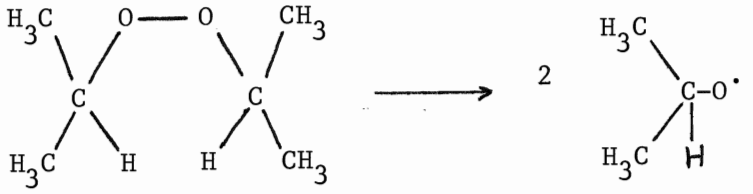
Type 1 homolysis has no particular conformational requirements for the transition state and so can readily accomodate to the preferred dihedral angle of 100° to 120° of the O-O bond(48).

Type 2 decomposition has a transition state which should be favored by a trans or near trans orientation of the peroxide substituents (50).

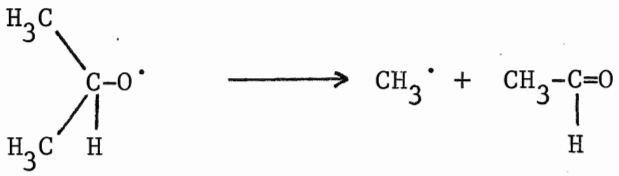
From the structural information we can see Type 3 reactions can occur when dihedral angle of either approximately 0° (which is unfavorable because of the eclipsed non-bonding orbitals) or by an angle of approximately 60° (pseudo chair form) which should be preferred for this type of transition state (48, 51). The barrier to internal rotation for H_2O_2 through the cis configuration in the vapor phase is about 7.0 Kcal/mole (50) which is comparable to the magnitude of the effects we are trying to explain. Conformation of cyclic peroxides has additional restrictions, these will be considered in a later section dealing with the result of 1,2 dioxane decomposition.

5.6 Product studies from decomposition of isopropyl peroxide

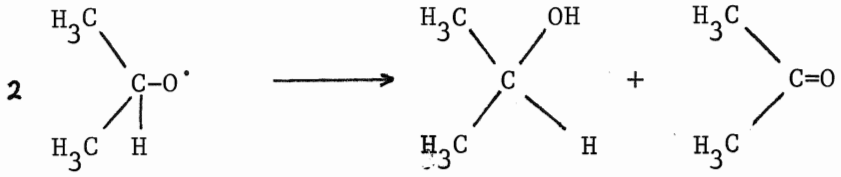
Product studies have been carried out in the four solvents at 140°C only (Table 6). In toluene the main products obtained were acetaldehyde, acetone, isopropyl alcohol, hydrogen, methane, carbon monoxide and bibenzyl. The reactions can be represented in radical terms as follows:



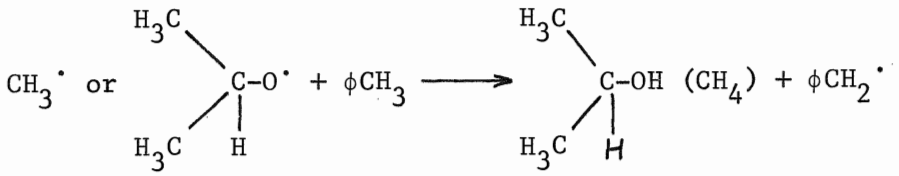
(5.6.1)



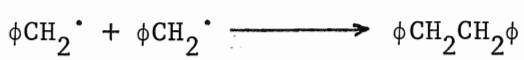
(5.6.2)



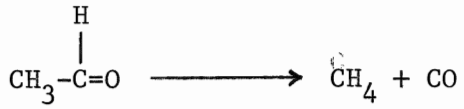
(5.6.3)



(5.6.4)

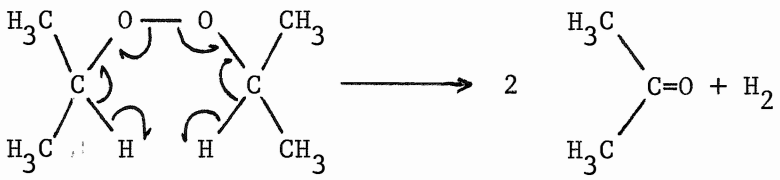


(5.6.5)



(5.6.6)

The high yield of bibenzyl and $(CH_3)_2CHOH$ (Table 6) shows that this radical mechanism is the major pathway. H_2 has been produced by the concerted path.

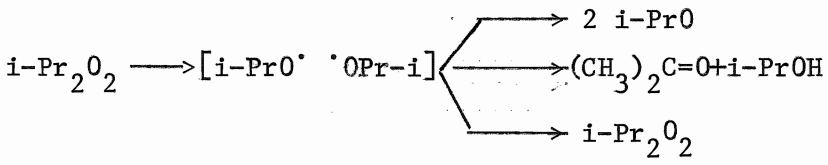


(5.6.7)

The low yield of H_2 shows this process is a minor pathway. Increasing temperature from 130° to 150°C the H_2 yield decreases from ∿ 9% to 5.6%. This in a way agrees with the proposed concerted mechanism; since the concerted pathway requires less energy than homolysis so the hydrogen yield should be higher at lower temperatures. This phenomonon also can be seen in other solvents used (Table 7).

5.7 Reactions of alkoxy radicals in toluene

The alkoxy radicals initially formed within the solvent cage could do any of three things; (1) diffuse apart and out of solvent cage (2) disproportionate within the cage and (3) recombine to form $i\text{-}pr_2o_2$ within the cage.



(5.7.1)

We cannot measure cage recombination, however, cage disproportionation can be estimated by determination of the percentage of the radicals escaping from the solvent cage as measured by the yield of solvent dimer (bibenzyl), and other consideration. That is, in toluene at 140°C the per cent of $i\text{-}Pr_2o_2$ going to radical products is 92.5. The yield of bibenzyl is 51%, so that at least 51/92.5 or 55% of the radicals escape from the solvent cage. However, a much lower maximum value for cage disproportionation is found by considering the yield of acetone, a necessary product from the disproportionation. If acetone is produced only by the concerted reaction, (for each H_2

count two acetones) or by cage disproportionation then the value for the latter becomes 26.6%. Even this number may be much too high if other mechanisms for producing acetone are important. Thus Hiatt et al (7a) using deuterium isotope labelling in the thermal decomposition of sec-butyl peroxide in toluene found much of the 2-butanone to result from benzyl radical-S -BuO· radical disproportionation. So it may be that some of the acetone comes from interaction of benzyl and i-PrO· radicals.

Carbon monoxide and some CH_4 come from decomposition of acetaldehyde.

$$CH_3CHO + R^{\cdot} \longrightarrow RH + CH_3\dot{C}{=}O \qquad (5.7.2)$$

$$CH_3\dot{C}{=}O \longrightarrow CH_3^{\cdot} + CO \qquad (5.7.3)$$

Substracting % CO from % CH_4 should represent the amount of CH_4 which is produced from β cleavage of i-PrO·.

5.7.1 Product studies in $(CH_3)_2CHOH$, MeOH and H_2O

Products of decomposition in $(CH_3)_2CHOH$ are essentially the same in quality as in toluene but not in quantity. Induced decomposition can be seen from the product balance (Table 6). Very little acetaldehyde has been formed whereas the yield of acetone is far greater than could come from i-PrOH, and is a product of solvent oxidation. Decomposition of isopropyl peroxide in isopropyl alcohol can be represented by the following mechanism.

$$(CH_3)_2CH\text{-}O\text{-}O\text{-}CH(CH_3)_2 \longrightarrow 2\ (CH_3)_2CHO^{\cdot} \qquad (5.7.4)$$

$$(CH_3)_2CHO^{\cdot} \longrightarrow CH_3CHO + CH_3^{\cdot} \qquad (5.7.5)$$

$$(CH_3)_2CHO\cdot \; (CH_3\cdot) + \underset{\text{SOLVENT}}{(CH_3)_2CHOH} \longrightarrow (CH_3)_2CHOH + \underset{\text{FROM SOLVENT}}{(CH_3)_2\dot{C}OH} \qquad (5.7.6)$$

$$(CH_3)_2CHO\cdot + (CH_3)_2CH\text{-}O\text{-}O\text{-}CH(CH_3)_2 \longrightarrow (CH_3)_2C{=}O + \underset{\text{FROM SOLVENT}}{(CH_3)_2CHOH} + (CH_3)_2CHO\cdot \qquad (5.7.7)$$

$$\underset{\text{FROM SOLVENT}}{(CH_3)_2CHO\cdot} + (CH_3)_2CHO\cdot \longrightarrow (CH_3)_2C{=}O + \underset{\text{FROM SOLVENT}}{(CH_3)_2CHOH} \qquad (5.7.8)$$

This mechanism shows why the yield of CH_3CHO is so low. Disproportionation between i-PrO$\cdot$ derived from solvent and that from peroxide is more favorable over β scission of i-PrO$\cdot$ derived from peroxide to form CH_3CHO and $CH_3\cdot$. The low yield of H_2 in $(CH_3)_2CHOH$ in spite of the solvent's higher polarity is due to the induced decomposition.

Decomposition of isopropyl peroxide in MeOH must not be very complicated by induced decomposition, since formaldehyde which would be an induced decomposition product, is found in only a trace amount. $H\text{-}\underset{\displaystyle H}{\underset{|}{C}}{=}O$ can be produced by the following mechanisms,

$$(CH_3)_2CH\text{-}O\text{-}O\text{-}CH(CH_3)_2 \longrightarrow 2\ (CH_3)_2CHO\cdot \qquad (5.7.9)$$

$$(CH_3)_2CHO\cdot \longrightarrow CH_3CHO + CH_3\cdot \qquad (5.7.10)$$

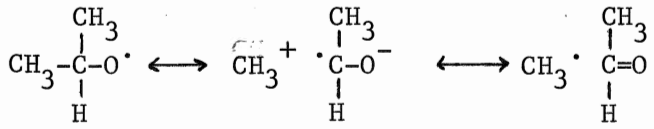
$$(CH_3)_2CHO\cdot \; (CH_3\cdot) + H\text{-}CH_2OH \longrightarrow (CH_3)_2CHOH + \cdot CH_2OH \qquad (5.7.11)$$

$$\cdot CH_2OH + (CH_3)_2CH\text{-}O\text{-}O\text{-}CH(CH_3)_2 \longrightarrow H\text{-}\underset{\displaystyle H}{\underset{|}{C}}{=}O + (CH_3)_2CHOH + (CH_3)_2CHO\cdot \qquad (5.7.12)$$

$$\cdot CH_2OH + (CH_3)_2CHO\cdot \longrightarrow H\text{-}\overset{\displaystyle H}{\overset{|}{C}}{=}O + (CH_3)_2CHOH \qquad (5.7.13)$$

Also, if induced decomposition was important the H_2 yield would decrease, whereas 30.5% hydrogen was found in MeOH at 140°C (Table 7).

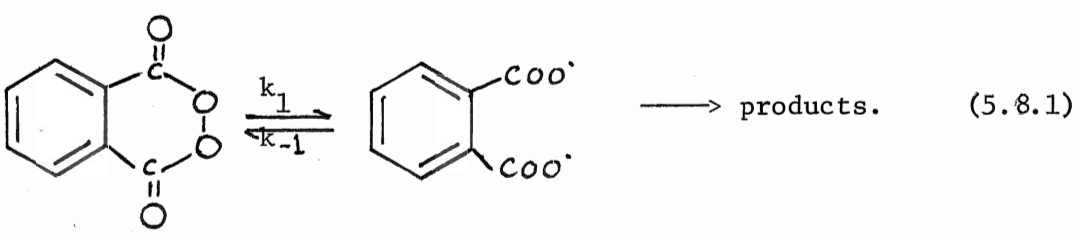
Decomposition of peroxide in water also produces mainly acetone, H_2, acetaldehyde, isopropyl alcohol, carbon monoxide and CH_4. The high yield of acetone parallels the high yield of H_2. High yield of CH_3CHO in H_2O may be due to the fact that β scission is more favorable in more polar solvents relative to hydrogen abstraction (52), since in this process bond breaking to give a relatively polar product is well underway.



(5.7.14)

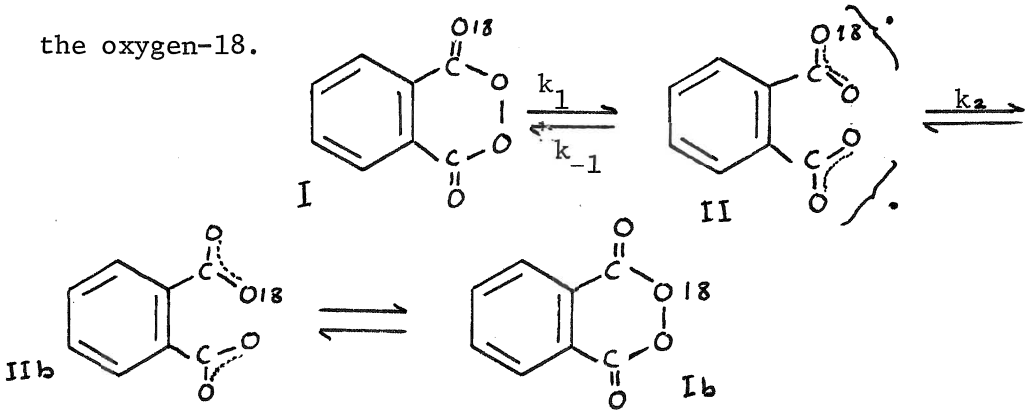
5.8 Thermal decomposition of cyclic peroxides

Thermal decomposition of phthaloyl peroxide has been studied in detail by F. D. Greene and co-workers (53). They found a great difference in its behavior from that of the diacyl peroxide (benzoyl peroxide). The induced decomposition in benzene and the "acid catalyzed" decomposition are prominent to a far greater degree than obtained for benzoyl peroxide, and the reaction with olefines is much faster in the acyclic analogs. This behavior has been explained in terms of an element of strain in the diacyl ring ascribed to the repulsion between the non-bonding electron pairs of peroxy-oxygen atoms. Also, the $-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}$ grouping of phthaloyl peroxide is more exposed and consequently more subject to attack than in the corresponding grouping in the acyclic analogs. Surprisingly, the decomposition of this peroxide in carbon tetrachloride is about 57 times slower than benzoyl peroxide. They suspected that this apparent stability may be the result of the follo wing equilibrium,



(5.8.1)

but oxygen-18 labelling (54) experiments showed only 11% scrambling of the oxygen-18.

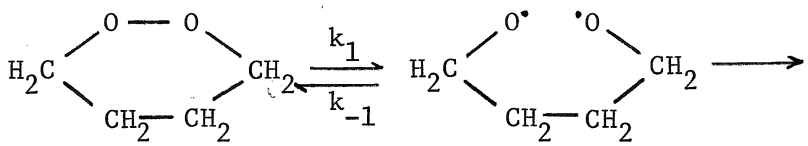


(5.8.2)

i.e., the conversion of Ia and Ib is unimportant under the experimental conditions. Greene therefore suggested that the greater stability of phthaloyl peroxide may lie in the fact that -O-O- bond fission of an of an acyclic peroxide may be achieved by a simple stretching of oxygen-oxygen bond whereas the related rupture in phthaloyl peroxide could be achieved only by twisting of the carbonyl carbon to ring carbon bonds. In contrast to this stability in CCl_4 K.E. Russell(55) found the activation energy for radical cleavage of -O-O- bond of phthaloyl peroxide in toluene to be about 25 Kcal/mole which is 8-10 Kcal/mole below that of open-chain peroxides. He explained this lower Ea in terms of the strained ring system. It will be noted that Greene's and Russell's results and explanations are contradictory. The disagreement has not been explained.

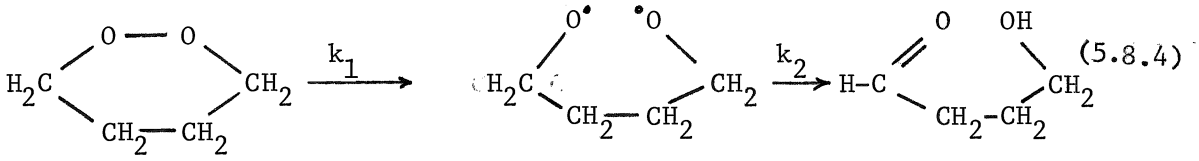
5.8.1 Decompositions of 1,2 dioxane

Our kinetic results from decomposition of 1,2-dioxane in t-butylbenzene (Table 5) shows an activation energy of 33.4 Kcal/mole. This activation energy is also much lower, however, and 1,2 dioxane decomposed less rapidly than i-pr_2o_2. A possible explanation is ring strain, perhaps coupled with opening and reclosing.



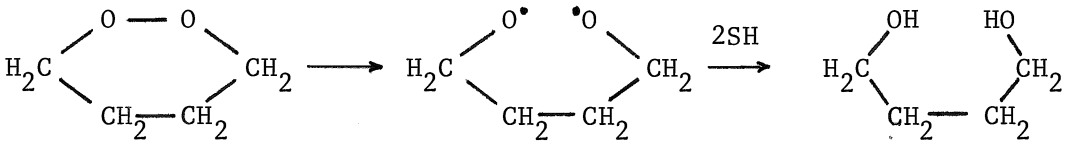
(5.8.3)

Product studies were carried out only in ϕCH_3 and in MeOH. Decomposition in ϕCH_3 did not produce appreciable amounts of H_2. It was concluded that the conformational requirement for H_2 formation is not satisfied and possibly this is due to the strain of the ring. The only product which could be identified in decomposition of 1,2 dioxane in ϕCH_3 was $HO(CH_2)_3CHO$ which might be obtained by the following mechanism.



(5.8.4)

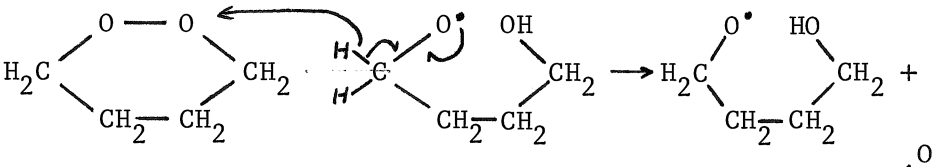
Second step shows disproportionation between two ends of the diradical. Attempts to find traces of bibenzyl and of 1,4 butanediol failed. These products could have beenobtained by the following mechanism,



(5.8.5)

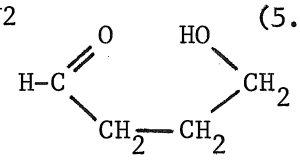
$S^{\cdot} + S^{\cdot} \longrightarrow S\text{-}S$

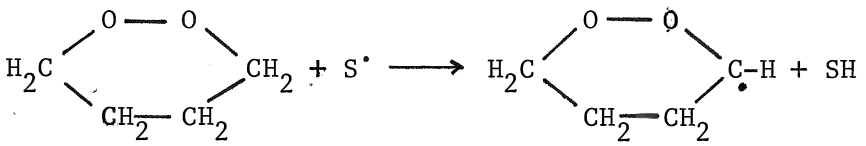
Induced decompositions could also explain the products



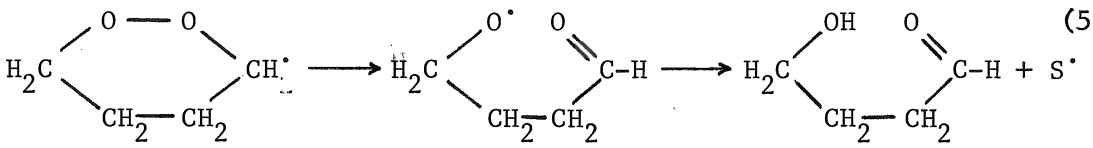
(5.8.6)

or,





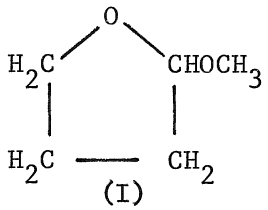
(5.8.7)



(5.8.8)

Kinetic studies in MeOH at 140° did not follow first order reaction in peroxide (Figure 10). In fact the decomposition was mildly autocatalytic.

Product studies in this solvent showed a single major product, identified as α-methoxy tetrahydrofuran (I) by g.c./M.S.



(I)

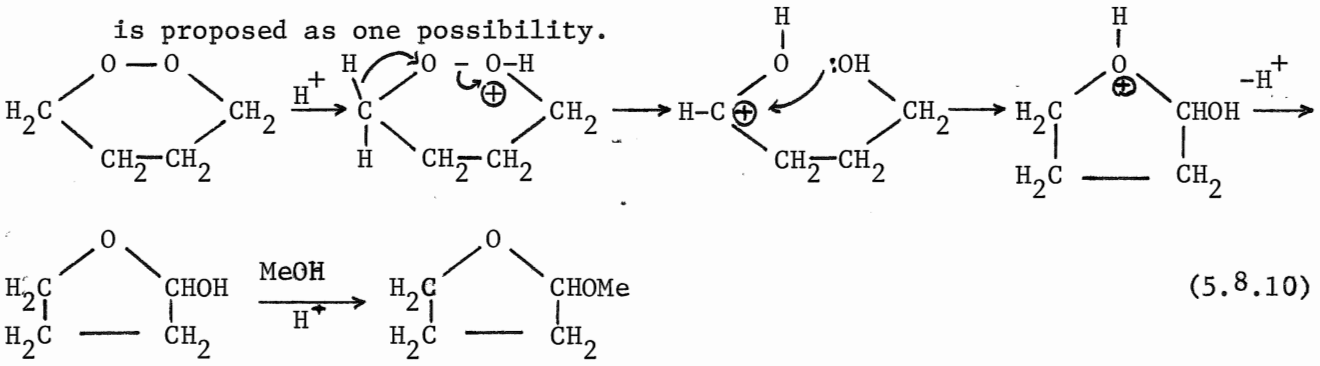
A rough quantitative estimation of its yield was made by comparing the peak areas for peroxide and (I) obtained by g.l.c. (flame ionization detector). Since the response in F.I.D. detector is proportional to the number of carbon atoms and in this case the number of carbon atom in peroxide and product are different by one. From the peak areas it was clear that the yield of (I) was quantitative. Another product with low molecular weight was found in very low yield, and was identified by g.c./M.S. as dimethyl ether. The production of methyl ether from methanol strongly suggested acid catalysis, and generation of trace quantities of acid could explain the autocatalytic nature of the 1,2 dioxane decomposition in methanol.

Acid catalyzed decomposition of alkyl peroxides is very common in presence of added acid. For instance,

$$t\text{-}BuO_2Cph_3 \xrightarrow[phH]{H^+} t\text{-}BuOH + ph_2c{=}O + phOH \qquad (5.8.9)$$

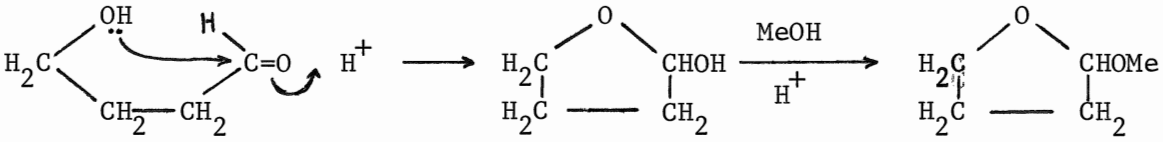
where the $phSO_3H$ is a catalyst (56), or acid catalyzed decomposition of α-cumyl peroxide in acetic acid with the addition of a small amount of perchloric acid (57). Since we conducted decomposition of 1,2dioxane in pure methanol we did not expect acid catalyzed decomposition. The apparent extreme sensitivity of 1,2 dioxane to acid may be due to the ring strain. The following

is proposed as one possibility.



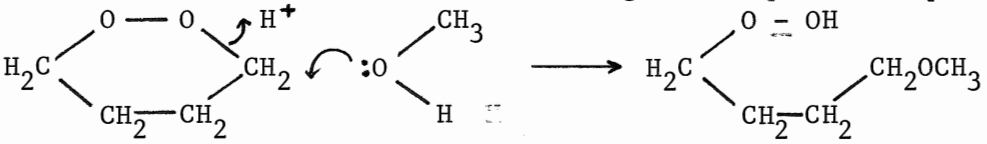
(5.8.10)

Another possibility is that 4-hydroxybutanal is formed in the usual free-radical way and the cyclizes as it certainly would do in methanol with acid catalysis.



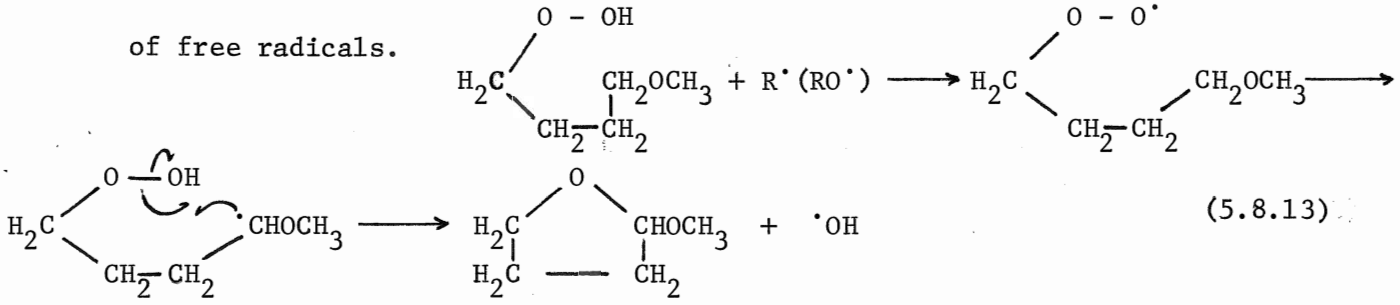
(5.8.11)

A more interesting third alternative is that 1,2-dioxane is sufficiently strained and unhindered to undergo nucleophilic displacement.



(5.8.12)

Cyclization of this hydroperoxide would occur readily in the presence of free radicals.



(5.8.13)

No choice can be made from these possibilities in the absence of further data.

At 140°C decomposition of 1,2-dioxane in CH_3OH up to complete decomposition produced even less H_2 than it decomposition in toluene. So, polar effects were not measurable due to the low H_2 yield in both solvents.

6. Conclusion

The mechanisms of decomposition of alkyl peroxides, or generally speaking, (Type 3) decompositions which show preference for liquid phase have been successfully examined.

The dependence of the rate of hydrogen production in decomposition of isopropyl peroxide on solvent polarity can be explained in terms of two possibilities.

1. Solvent stabilizes the six-centered transition state which possesses considerable ionic character as represented in (I), (II).
2. Solvent stabilizes the required conformation for this process. We can not distinguish between the two possibilities in the absence of more evidence, but can make a generalization that the presence of solvent increases the reaction rate of the cyclic concerted Type 3 decomposition, so that in the liquid phase, but not in gas phase, this non-radical mode of decomposition predominates over homolytic cleavage.

Unfortunately the decomposition of 1,2-dioxane in toluene and methanol produced very little of H_2 to measure the polar effect which could lead us to more conclusions of the conformational effect on decomposition of Type 3.

Lower activation energy found for decomposition of 1,2-dioxane in tert-butylbenzene (33.4 Kcal/mole) compared with that of isopropyl peroxide 39.1 Kcal/mole in toluene, can be attributed to the ring strain due to the repulsion of the non-bonding electrons on oxygens. No decision can be made for the possibilities of the reclosing of the 1,2-dioxane once it ruptured by results of this work.

Products of decomposition of 1,2-dioxane in toluene can be explained by two mechanisms, (1) disproportionation between the two ends of the diradical, (2) radical induced decompositions.

Products of decomposition of 1,2-dioxane in methanol can be explained

by three mechanisms, (1) acid catalyzed decomposition of 1,2-dioxane, (2) acid catalyzed decomposition of 4-hydroxybutanal, and (3) nucleophilic displacement. Further work is required before making any choice between these possibilities.

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Appendix (I)

Analysis of isopropyl peroxide for kinetic studies

The sealed ampoules taken from the oil bath at appropriate intervals were first analysed for remaining i-pr_2O_2 by gas chromatography. Columns and conditions in different solvents are given below.

Rate measurement in ϕCH_3

Column dimensions	6 ft, 1/8" stainless steel.
Packing	5% SE-30 on Chromosorb W 80-100 mesh
Column temperature	58°C
Injector temperature	35-40°C
Carrier gas	Helium 25 ml/min.
Detector	F. I. D.

Retention times (min)

i-pr_2O_2	2.2
Toluene	3.5
(I.S)Nonane	9

I.S. = Internal Standard

This column is unable to separate i-prOH from $(CH_3)_2CO$. Another column which did not decompose the peroxide and could separate all the peaks, was di-isodecyl phthalate.

Column	6 ft., 1/8" teflon
Packing	10% di-isodecyl phthalate on Chromosorb W 80-100 mesh
Column temperature	55°C
Injector temperature	40°C
Carrier gas	Helium 20 ml/min.

Retention times (min)

i-pr_2O_2	4.3
(I.S.) octane	6.5
toluene	11

Rate study in isopropyl alcohol

Column	10 ft, 1/8" teflon
Packing	10% di-isodecyl phthalate on Chromosorb W
Column temperature	52°C
Injector temperature	40°C
Carrier gas	Helium 20 ml/min.

Retention times (min)

i-pr_2O_2	11
i-prOH	5.5
(I.S.) pentane	2.5

Rate study in MeOH

Column	6 ft, 1/8" stainless steel
Packing	15%, SE-30 on Chromosorb W 80-100 mesh
Column temperature	55°C
Injector temperature	40°C
Carrier gas	Helium 20 ml/min.

Retention Times (min)

MeOH	0.91
i-pr_2O_2	7
(I.S.) octane	18

MeOH tails badly on this column but does not interfere with analysis.

Kinetic study in H_2O

Kinetic and products study in H_2O was rather troublesome since i-pr_2O_2 is not very soluble in H_2O. Secondly injection of water in column will cause damage to the packing material so after a few injections the column needs to be repacked. Finally because of the low concentration of the peroxide, it is necessary to use high sensitivity in instrument which causes drifting of the base line. The analysis was carried out under the following conditions.

Column	10 ft, 1/8" teflon
Packing	10% di-isodecyl phthalate
Column temperature	55°C
Injector temperature	40°C
Carrier gas	Helium 25 ml/min
Retention times	
(I.S.) M. E. K.	7.5
i-pr_2O_2	10

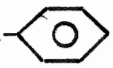
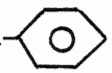
Analysis of 1,2-dioxane for Kinetic studies

Kinetic studies of 1,2-dioxane in toluene were not done since it proved impossible to separate 1,2-dioxane from toluene by gas chromatography. The only column which could separate them was 20% Carbowax 1500, but peroxide suffered decomposition on this column.

Columns which could not separate toluene from 1,2-dioxane

1. 5% SE-30 (6 ft, 12 ft, 1/8" and 6 ft 1/4") on Chromosorb W 80-100 mesh
2. 5% QF-1 (" ") "
3. 20% FFAP (" ") "

4. 10% di-isodecyl phthalate (7 ft, 10 ft, 1/8") on Chromosorb W 80-100 mesh
5. 5% Silicon D.C.-200 (6 ft ") "
6. 20% Ethofat (6 ft ") "

Kinetics of 1,2-dioxane decompositions were studied in t-Buϕ between 140-170°C on column packed with 10% di-isodecyl phthalate. A trace amount of benzene existed as an impurity in the t-Bu-  which interferes with the peroxide on the column packed with 5% SE-30. t-Bu-  comes very late on the di-isodecyl phthalate column and it was necessary after each injection to increase the column temperature to 120°C. After elution of the t-Bu-  the column was cooled again. Since the ratio of internal standard to peroxide was measured in each injection there would be no error due to the changing of the column conditions if any such occurred.

Column	7 ft, stainless steel
Packing	10% di-isodecyl phthalate
Column temperature	60°C
Injector temperature	40°C
Carrier gas	Helium 25 ml/min
Retention times (min)	
Benzene	5
1,2-dioxane	13
t-Bu-	late

Kinetic studies of 1,2-dioxane in MeOH

Column	10 ft, 1/8" teflon
Packing	10%, di-isodecyl phthalate
Column temperature	75°C

Injector temperature	75°C
Carrier gas	Helium 40 ml/min
Detector	F. I. D.
Retention times (min)	
MeOH	1.5
1,2-dioxane	12.3
α-methoxy tetrahydrofuran	9.2
(I.S.) nonane	19.5

Appendix (II)

Analysis of the liquid products of decomposition of isopropyl peroxide in toluene

All the liquid products were analysed on 7 ft, 10% di-isodecyl phthalate, on which all components could be separated nicely. Peroxide does not decompose on this column. All peaks are sharp and symmetrical except for toluene which tails. For quantitative analysis octane was used as internal standard. Conditions are given below.

Column	7 ft, teflon
Packing	10% di-isodecyl phthalate on Chromosorb W 80-100 mesh
Column temperature	55°C
Injector temperature	78°C
Carrier gas	Helium 20 ml/min

Retention times (min)

CH_3CHO	1.3
CH_3COCH_3	2.15
$(CH_3)_2CHOH$	2.8
octane	4.3
toluene	11.7

Bibenzyl was analysed on 20% Apiezon N on Chromosorb P 60-80 mesh at column temperature 180°C and flow rate 25 ml/min.

Retention times (min)

ϕCH_3	0.5
$(C_6H_5CH_2)_2$	11.3
(I.S.) hexadecane	13.8

Product studies in decomposition of isopropyl peroxide in MeOH and $(CH_3)_2CHOH$

The quantitative analysis of the products from decomposition in MeOH and $(CH_3)_2CHOH$ was carried out on a 6 ft column packed with 20% carbamon 1500 on Chromosorb W 80-100 mesh in the following conditions

Column temperature	35°C
Injector temperature	100°C
Carrier gas	Helium 20 ml/min.
Retention times (min)	
CH_3CHO	2
CH_3COCH_3	4.9
Nonane (I.S.)	6.8
MeOH	12.6
$(CH_3)_2CHOH$	16.3

Since CH_3CHO tails on carbowax 1500 its analysis was carried out on 6 ft, 10% Ethofat on Chromosorb W 80-100 mesh under the following conditions

Column temperature	50°C
Injector temperature	85°C
Carrier gas	Helium 20 ml/min
Retention times (min)	
CH_3CHO	1.1
$(CH_3)_2C=O$	2
MeOH	3.3
$(CH_3)_2CHOH$	4.6
Nonane	11.1

Products studies from decomposition in H_2O

Liquid products were analysed on a 7 ft column packed with 10% di-isodecyl phthalate on Chromosorb W and a flow rate of 25 ml/min at 55°C column temperature.

Retention times

CH_3CHO	1
$(CH_3)_2CO$	1.7
$(CH_3)_2CHOH$	2.2
M. E. K. (I. S.)	3.4